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CHEMICAL ATTENUATION OF MAJOR AND TRACE ELEMENTS AND RADIONUCLIDES IN PHOSPHOGYPSUM SLUICE WATER

BY

JAMES KEVIN BALL ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Masters of Science.

IN

SOIL CHEMISTRY

DEPARTMENT OF SOIL SCIENCE

EDMONTON, ALBERTA

FALL 1994

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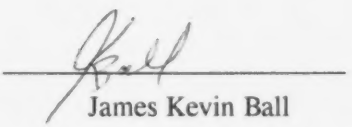

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M. J. Dudas (Supervisor)

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D.C. Sego

Date: June 2, 1994

For my family

Abstract

Phosphogypsum (PG), a by-product of the manufacture of phosphate fertilizer, is presently produced and/or stockpiled within the province of Alberta. Processing of rock phosphate during phosphate fertilizer production results in waste streams (sluice water) that contain elevated levels of radionuclides and environmentally sensitive major and trace elements particularly U^{238} (3.5 mgL^{-1}), SO4 (8600 mgL^{-1}), F (4700 mgL^{-1}), H (pH 1.6), As (1.3 mgL^{-1}), Cd (2 mgL^{-1}), Cr (1.8 mgL^{-1}), and Se (0.7 mgL^{-1}). The objective of this work was to determine how soluble levels of these elements decrease in response to chemical neutralization and reaction with soil clays. Batch experiments were carried out in which the initial acidic sluice water was 1) incrementally neutralized with $Ca(OH)_2$ and 2) reacted with a clay rich soil horizon. Solution concentration data showed that attenuation may not be enough to reduce sulfate levels below regulatory limits. The geochemical reactions indicate there is potential for subsurface migration of fluoride at 13 mgL^{-1} even after attenuation. Uranium will only be mobile for strong acid conditions. Arsenic, cadmium and chromium are effectively reduced below regulatory limits at pH >5. Selenium may be problematic. Outside the pH range 3.5 to 6, Se could be mobile and become an environmental problem at concentrations of about 0.25 mgL^{-1}. The conclusions of this study apply tc the Alberta environment because of the abundance of carbonates and clay minerals in subsoils. The generic nature of this study also provides geochemical information on attenuation that should be useful for other environments and even for other acid wastes containing a variety of trace elements.

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TABLE OF CONTENTS

CHAPTER I INTRODUCTION 1

CHAPTER II LITERATURE REVIEW 3

A. INTRODUCTION 3

B. PHOSPHATE ORE: AN OVERVIEW 3

C. PHOSPHATE ROCK: ITS ORIGIN AND CHEMISTRY 8

D. PLANT OPERATION 10

1. Site Layout 10

2. Processing 10

E. WASTE MANAGEMENT 12

1. Management to prevent groundwater contamination 13

2. Prevention of surface runoff 14

3. Leaching 15

4. Use of drains, ditches, and interceptor wells 15

5. Use of liners 15

6. Neutralization as control 16

F. ELEMENTS OF CONCERN 17

1. Major elements 18

FLUORIDE 18

2. Radionuclides 19

i. URANIUM 19

ii. THORIUM 20

iii. LEAD 20

iv. RADIUM 20

3. Trace elements 21

i. ARSENIC 21

ii. CADMIUM 21

iii. CHROMIUM 22

iv. SELENIUM 22

G. SUMMARY 23

CHAPTER III MATERIALS AND METHODS 24

A. PHOSPHOGYPSUM SLUICE WATER 24

1. Sampling 24

2. Material treatment 24

3. Initial analysis 24
B. SOIL 25
1. Sampling 25
2. Material treatment 25
3. Initial analysis 25
C. EXPERIMENTAL SET-UP 27
1. Chemical neutralization 27
2. Soil adsorption 29
3. Evaporation experiment 29
D. ANALYSIS 31
1. Gamma-emitting radionuclides 31
2. Chemical analysis 32
3. Routine analysis 34
4. Computer modelling 34
CHAPTER IV RESULTS AND DISCUSSION 35
A. INITIAL ANALYSIS 35
1. pH 35
2. Electrical conductivity 35
3. Chemical constituents 36
i. MAJOR ELEMENTS 37
ii. RADIONUCLIDES 37
iii. TRACE ELEMENTS 39
B. ELEMENTAL CHEMISTRY, SOLUBILITY EQUILIBRIA, AND COMPUTER SPECIATION 40
1. Major elements 41
i. CALCIUM 41
ii. SULFATE 44
iii. PHOSPHORUS 46
iv. IRON 46
v. FLUORIDE PRECIPITATION 49
vi. FLUORIDE ADSORPTION 52
2. Radionuclides 54
URANIUM 54
3. Trace elements 59
i. ARSENIC PRECIPITATION 59
ii. ARSENIC ADSORPTION 63

iii. CADMIUM PRECIPITATION 65
iv. CADMIUM ADSORPTION 68
v. CHROMIUM PRECIPITATION 70
vi. CHROMIUM ADSORPTION 74
vii. SELENIUM PRECIPITATION 77
viii. SELENIUM ADSORPTION 81

CHAPTER V SUMMARY AND CONCLUSIONS 85

REFERENCES 88

LIST OF TABLES

Table 1. Concentrations of trace elements in marine phosphorites relative to shale (mg/kg). 5

Table 2. Average trace element concentrations of selected marine phosphorite deposits (mg/kg). 7

Table 3. Sluice water contaminant values with reference to drinking water guidelines (mg/L). 17

Table 4. Chemical and physical soil properties of Orthic Gray Luvisol Bt horizon soil. 26

Table 5. Physical, elemental, and mineralogical analysis of clay used in soil adsorption experiment Soil is Bt horizon Orthic Gray Luvisol. 27

Table 6. Correction factors (CF) for adsorption experiment as a result of evaporation losses. 31

Table 7. Table of elemental analysis techniques used and detection limits. 33

LIST OF FIGURES

Figure 1. Location of the Togo phosphate rock deposits in Africa. 9
Figure 2. Schematic section of the Togo deposits showing(A) in the basin and (B) the deposit. 9
Figure 3. Plant site, Central Alberta, Canada. 11
Figure 4. Phosphate plant filter diagram identifying route of phosphoric acid. 12
Figure 5. Amounts of $Ca(OH)_2$ required vs. pH value of sluice water. 28
Figure 6. Partitioning of contaminants between solid and liquid phase. 36
Figure 7. Gamma spectrum for phosphogypsum sluice water. 38
Figure 8. Gamma Spectrum for distilled water background sample. 38
Figure 9. Soluble calcium concentration (mg L^{-1}) versus change in pH. 42
Figure 10. Gypsum solubility equilibrium with neutralization experiment data. 43
Figure 11. Solubility equilibria of some calcium minerals with neutralization data. 43
Figure 12. Soluble sulfate concentration (mg L^{-1}) versus change in pH. 45
Figure 13. Adsorption curve for sulfate in relation to solution pH. 45
Figure 14. Soluble phosphorous concentration (mg L^{-1}) versus change in pH. 47
Figure 15. Soluble iron concentration (mg L^{-1}) versus change in pH. 47
Figure 16. Solubility equilibria of some iron minerals with neutralization data. 48
Figure 17. Soluble fluoride concentration (mg L^{-1}) versus change in pH. 50
Figure 18. Solubility equilibria of some fluoride minerals with neutralization data. 51
Figure 19. GEOCHEM predicted speciation of fluoride following neutralization. 51
Figure 20. Adsorption curve for fluoride in relation to solution pH. 53
Figure 21. GEOCHEM predicted speciation of fluoride following adsorption. 54
Figure 22. Soluble U-238 activity (Bq L^{-1}) versus change in pH. 55
Figure 23. Soluble U-238 concentration (mg L^{-1}) versus change in pH. 56
Figure 24. Soluble uranium concentration (mg L^{-1}) versus change in pH. 56

Figure 25. GEOCHEM predicted speciation of uranium following neutralization. 57
Figure 26. GEOCHEM predicted speciation of uranium following neutralization. 58
Figure 27. Adsorption curve for uranium in relation to solution pH. 58
Figure 28. GEOCHEM predicted speciation of uranium following adsorption. 59
Figure 29. Soluble arsenic concentration (mg L^{-1}) versus change in pH. 60
Figure 30. Solubility equilibria of some arsenate minerals with neutralization data. 61
Figure 31. GEOCHEM predicted arsenic of arsenic following neutralization. 62
Figure 32. GEOCHEM predicted arsenic of arsenic following neutralization. 63
Figure 33. Adsorption curve for arsenic in relation to solution pH. 64
Figure 34. GEOCHEM predicted speciation of arsenic following adsorption. 64
Figure 35. GEOCHEM predicted speciation of arsenic following adsorption. 65
Figure 36. Soluble cadmium concentration (mg L^{-1}) versus change in pH. 66
Figure 37. Solubility equilibria of some cadmium minerals with neutralization data. 67
Figure 38. GEOCHEM predicted speciation of cadmium following neutralization. 68
Figure 39 Adsorption curve for cadmium in relation to solution pH. 69
Figure 40. GEOCHEM predicted speciation of cadmium following adsorption. 70
Figure 41. Soluble chromium concentration (mg L^{-1}) versus change in pH. 72
Figure 42. Solubility equilibria of some chromium minerals with neutralization data. 72
Figure 43. GEOCHEM predicted speciation of chromium following neutralization. 73
Figure 44. GEOCHEM predicted speciation of chromium following neutralization. 74
Figure 45. GEOCHEM predicted speciation of chromium following neutralization. 74

Figure 46. Adsorption curve for chromium in relation to solution pH. 75
Figure 47. GEOCHEM predicted speciation of chromium following adsorption. 76
Figure 48. GEOCHEM predicted speciation of chromium following adsorption. 77
Figure 49. GEOCHEM predicted speciation of chromium following adsorption. 77
Figure 50. Soluble selenium concentration (mg L^{-1}) versus change in pH. 78
Figure 51. Solubility equilibria of some biselenite minerals with neutralization data. 80
Figure 52. GEOCHEM predicted speciation of selenium following neutralization. 81
Figure 53. Adsorption curve for selenium in relation to solution pH. 82
Figure 54. GEOCHEM predicted speciation of selenium following adsorption. 83

CHAPTER I

INTRODUCTION

Phosphate fertilizer production is ongoing in both industrialized and third world countries around the world. Presently in Canada there are six phosphate fertilizer plants operating to produce as an intermediate, phosphoric acid. Phosphoric acid is the most important intermediate manufactured by the industry because it is an ingredient in every phosphate fertilizer except normal superphosphate (McBeath, 1987). The manufacturing of phosphoric acid yields waste by-products. Phosphogypsum, an acidic gypsum based waste, is one by-product. Other by-products include hydrofluoric acid and a variety of trace elements found in acid sludge and scrubber solids. The main by-product, phosphogypsum, is produced during the digestion of phosphate rock with sulfuric acid. For each ton of P_2O_5 produced approximately 4.5 - 5.5 tons of phosphogypsum are produced (Ferguson, 1988). World wide this equates to, as of 1983, 120 -150 million metric tons (mmt) of phosphogypsum produced annually, and if trends continue, 220 - 280 mmt by the year 2000 (Carmichael, 1988). Of these vast amounts of phosphogypsum produced approximately 14% is reprocessed, 58% is stored, and 28% is dumped (Carmichael, 1988). Due to the large amount of this material stored and dumped there is environmental concern as to the nature of the phosphogypsum as well as characterization of the leachate present at phosphogypsum stockpiles. Major environmental studies have been directed towards its discharge into aquatic environments and landfills. There are constant concerns about (1) the quality of the groundwater in the vicinity of the PG stacks, (2) contamination of groundwater at active sites from leaching process water, (3) runoff of the process water from the industrial site, and (4) by the long term contamination of the subsurface environment by infiltrating rain water after close out of a stack.

By examining the process sluice water directly one can gain generic information regarding contaminants that pose the most negative potential environmental impact. The sluice water itself contains the highest levels of soluble contaminants as well as the lowest pH. Characterizing the sluice water with respect to its contaminant levels and attenuation of these contaminants as it leaches through possible waste repository environments, including calcareous soil and clay layers, can provide information on the worst possible leaching scenarios.

This study was undertaken in order to gain information regarding the chemical attenuation of phosphogypsum process water (sluice water). The objectives of this study are to characterize the chemical composition of a typical Alberta phosphogypsum sluice water and to determine attenuation of selected dissolved constituents when sluice water is neutralized by reaction with a base and through sorption with soil minerals.

These studies are needed in order to elucidate the extent to which certain noxious trace elements (As, Cd, Cr, F, and Se) including radioactive elements (U) contained in the sluice water are chemically precipitated in soil and adsorbed by soil clays. The environmental impact of phosphogypsum sluice water will largely be determined by the nature and extent of these chemical attenuation mechanisms.

CHAPTER II

LITERATURE REVIEW

A. Introduction

The extent of pollution caused by the phosphate fertilizer industry is dependent upon many variables. The raw materials used, processing procedures utilized within the various plants, storage and handling of wastes, and the surrounding environments into which the wastes penetrate are all involved in determining potential environmental risk. Environmental risk can be resolved using two factors, i.e., the level of contaminants in the material, and the migration patterns of the various contaminants impacting on soil and aquatic environments.

The production of phosphoric acid can be attained via two routes: the wet process, and the electric furnace process. The electric furnace process is used only where elemental phosphorous is needed. Wet process accounts for over 90% of current phosphoric acid production (Becker, 1989). The production of phosphoric acid by wet process involves digesting rock phosphate with sulfuric acid and water to form gypsum, phosphoric acid, and minor amounts of hydrofluoric acid. The simplified reaction is:

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O \longrightarrow 5CaSO_4 \cdot 2H_2O + 3H_3PO_4 + HF$$

B. Phosphate Ore: An Overview

Commercial phosphate ores (rocks) have one property in common. Their phosphatic content consists of an apatitic structure of phosphate - fluorine - calcium combination. There are two types of phosphate ores, sedimentary and igneous, although sedimentary - phosphorites represent about 85% of the known phosphate rock origin (Habashi, 1980). Both types are associated with a large number of impurities. The source of the parent material plays an important role in the amounts of impurity present in the PG and it is concluded that the rock from igneous sources is much purer than that from sedimentary (Habashi, 1980). The general formula for apatite minerals is:

$$(Ca, Na_2, Mg)_{10}(PO_4)_{6-x}(CO_3)_xF_y(F, OH)_{2-y}$$

(where : y = 0.33x to 0.50x)

The quality of phosphoric acid and the level of contaminants is dependent on the raw materials used. Due to increases in demand original rock sources of high grade ore (Morocco, U.S.A., and U.S.S.R.) are no longer sufficient and new deposits are being mined with variations in quality and composition (Becker, 1989). New lower quality ores are now being exploited and there is little information on the levels of contaminants in these deposits.

The enrichment of a variety of trace elements and radionuclides in marine phosphorites has been documented. Altschuler (1980) categorizes trace elements as being either enriched, normal, or depleted relative to average shale. Shale is used as background rather than crustal abundance to gain a better baseline comparison with marine rocks.

Elements enriched in average phosphorite (Table 1) are Cd (60x), U (30x), Ag (30x), Y (10x), Se (8x), Yb (5x), Mo (4x), La (4x), Sr, Pb, and Zn (2x each). The elements of normal abundance are As, Ba, Be, Ce, Cr, Cu, Mn, Ni, Sc, and V. Of these elements the ones of major environmental concern are Cd, U, Se, As, and Cr. These patterns of enrichment have been attributed to substitution of trace elements for major elements, mainly calcium, in the apatite structure. There may also be other minerals associated with apatite and found in the phosphate rocks that contribute to enrichment. Metals and metalloids have also been found complexed and adsorbed to organics found in the phosphate rocks (Altschuler, 1980). These include Ag, Se, Mo, As, Ni, V, Zn, Cr, Cu, Cd, and Sb.

Major substitution and enrichment patterns evident in apatite structures include Cd, U, Sr, Pb, Zn, and Y replacing calcium. Carbonate, UO_2, AsO_4, and SO_4 also replace phosphate and Ag, Se, and Mo bind to organic matter.

Table 1. Concentrations of trace elements in marine phosphorites relative to shale (mg/kg).

	Average Shale	Average Phosphorite	Enrichment Factor	Normal Abundance	Depletion Factor
Ag	0.07	2	Ag 30		
As	13	23		As	
B	100	16			B 6
Ba	580	350		Ba	
Be	3	2.6		Be	
Cd	0.3	18	Cd 60		
Co	19	7			Co 6
Cr	90	125		Cr	
Cu	45	75		Cu	
Ga	19	4			Ga 5
Hg ppb	400	55			Hg 7
La	40	147	La 4		
Li	66	5			Li 13
Mn	850	1230		Mn	
Mo	2.6	9	Mo 4		
Ni	68	53		Ni	
Pb	20	50	Pb 2		
Sc	13	11		Sc	
Se	0.6	4.6	Se 8		
Sn	6	3			Sn 2
Sr	300	750	Sr 2		
Ti	4600	640			Ti 7
U	3.7	120	U 30		
V	130	100		V	
Y	26	260	Y 10		
Yb	2.6	14	Yb 5		
Zn	95	195	Zn 2		
Zr	160	70			Zr 2

Table adapted from Altschuler, 1980.

Phosphate ore is also naturally high in radioactivity from U-238 and Th-232 decay series. Different phosphate ores contain different levels of U and Th. Habashi (1980) found that sedimentary phosphates contain high U-238 decay series radionuclides and low Th-232, whereas phosphate rock of igneous origin contain low U-238 and high Th-232 decay series radionuclides. There is also enrichment patterns observed for radionuclides due to substitutions for major elements within the apatite structure. Uranium exists as U (IV) and substitutes for Ca within the apatite structure while U (VI) occurs as UO_2^{+2} and can be found adsorbed onto the apatite (Hurst and Arnold, 1980). Thorium exists in the +4 oxidation state and can substitute for Ca or occur as co-precipitates with Fe and Mn oxides as impurities in the phosphate rock. Thorium is in low levels in Togo sedimentary deposits so it is not of great environmental concern in this study. Radium as Ra-226 from the U-238 decay chain is also enriched in phosphate rock due to co-precipitation with Ba and/or Sr as sulfate compounds.

Table 1 shows the average levels of trace elements in phosphate rocks. There are vast differences in concentrations among the various rock sources. Data shown in Table 2 gives an indication of elemental variability among rock sources. Due to the wide range in contaminant levels there will also be a wide range in levels of contaminants in the processing products, phosphogypsum, process or sluice water, and phosphoric acid produced from these different rock sources.

There is limited information present in the literature on the trace element chemistry of phosphogypsum and/or sluice water from phosphoric acid plants that use Florida and Idaho rock phosphate and virtually none on plants utilizing Togo rock. Due to the differences in rock sources as well as differences within each rock source, information must be compiled on all rock sources.

Table 2. Average trace element concentrations of selected marine phosphorite deposits (mg/kg).

	Tamalyk Krasnoyarsk Siberia	Bone Valley Fm. Florida	Phosphoria Fm Rocky Mts. Idaho	Oulad Abdoun Basin Morocco/Togo
Ag	1	1.4	3	7
As	7.8	12	40	15
Ba	500	56	100	100
Cd	30	16	40	10
Co	-	4.5	2	-
Cr	90	60	1000	300
Cu	300	13	100	150
Hg	-	0.025	-	0.055
La	-	106	300	300
Mn	100	230	30	8
Mo	10	2.8	19	-
Ni	200	9	100	20
Pb	30	55	-	-
Se	-	2.6	13	2.5
Sc	-	6	10	10
Sr	300	1400	1000	1500
Ti	500	405	1000	200
U	-	140	90	140
V	70	70	300	70
Y	100	235	300	700
Yb	-	12	10	30
Zn	2500	180	300	215

Table adapted from Altschuler, 1980.

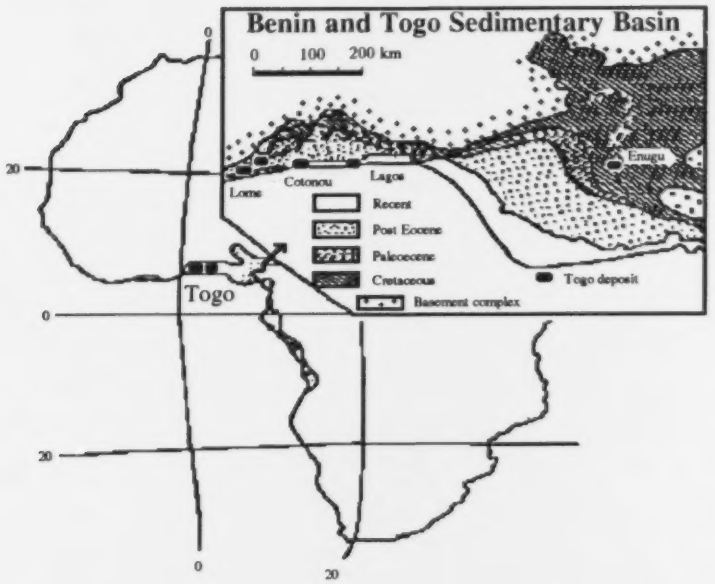
C. Phosphate rock: Its Origin and Chemistry

Phosphate ore utilized at one of three fertilizer manufacturing sites in Alberta originates predominantly from the phosphate deposits of Togo, western Africa (Fig. 1). Exploitation of the reserves in southern Togo began in 1961. The deposits contain Eocene sediments that form part of the large continental basin stretching from Ghana eastwards through Benin and into Nigeria (Fig. 2). The principle ore-bodies are situated at the towns of Kpogame and Hahatoe, respectively 25 and 35 km northeast of Lome, the capital of Togo.

The Togo deposits are worked by the Office Togolais des Phosphates (OTP). The deposits geological characteristics include a base of attapulgite bearing argillaceous laminites overlain by alternating sequences, several metres thick, of marls and phosphatic limestones rich in forminifera. There may also be beds of phosphatic and calcareous arenites several centimetres thick. The entire deposit is overlain by a marly clay rich in organic matter, algae, and dwarf microfauna. This makes up the footwall of the worked ore. Leading up to the worked ores is an area consisting of alternating sequences of phospharenites, calcareous limestones, and phosphatised marls.

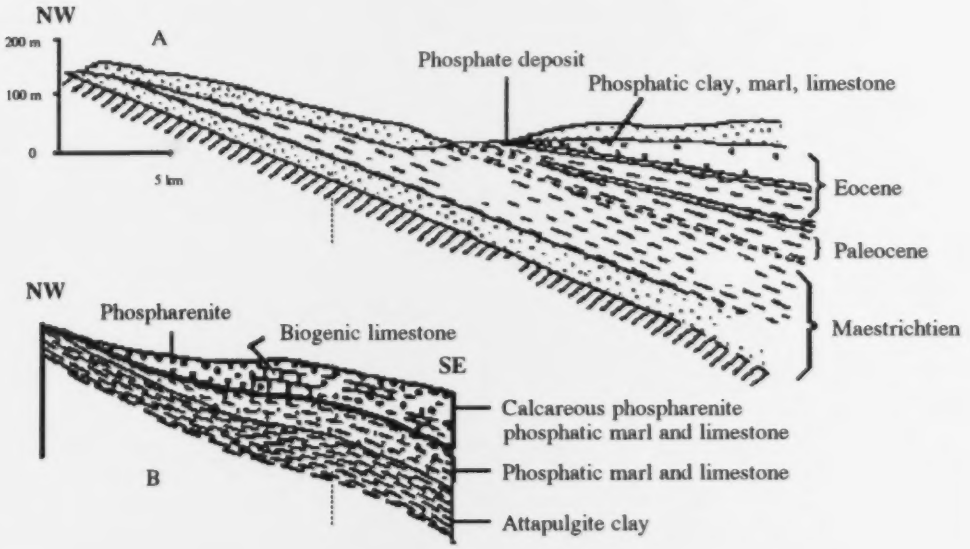
The exploited phospharenite is found in a cut off lagoon where the phosphate accumulated. This exploited area is a phospharenite with an argillaceous gangue. The Togo deposits form a belt NE - SW 30 km long whose width varies from a few hundred metres to more than 2 km. The phosphate deposit is 2 - 6 metres thick overlain by 7 metres of sand and approximately 30 metres of clay. Extraction involves bucket-wheel excavators at quarries at the two towns mentioned previously.

Most phosphate grains have a diameter of less than 200 um and includes the following analysis: P_2O_5 30.4%, CaO 40.6%, SiO_2 9.4%, Al_2O_5 10.2%, and Fe_2O_3 2.1% (Slansky, 1989). A high grade concentrate is produced for market by removing the argillaceous fraction during beneficiation at the place of mining. The beneficiated ore is carried via railway to Kpeme and loaded onto ships for delivery to Vancouver and then by railway to the Edmonton area.



Adapted from Slansky (1989)

Figure 1. Location of the Togo phosphate rock deposits in Africa.



Adapted from Slansky (1989)

Figure 2. Schematic section of the Togo deposits showing (A) the basin structure and (B) the deposit.

D. Plant Operation

1. Site Layout

The phosphate plant in central Alberta started operations in 1968 and is one of only two plants in operation in Alberta. The waste site consists of one main pond divided into 3 compartments or cells (Fig. 3). The production capacity of the plant is 900 tonnes/day P_2O_5 giving approximately $8.6x10^5$ m^3 yearly output of phosphogypsum waste. The stacks are located 15 kilometres from the nearest residential area and adjacent to the North Saskatchewan River. The topography is flat to gently undulating and the soil types which make up the area include Chernozemic soils of the Peace Hills Meadow and Peace Hills Loamy Fine Sand classification (Bowser, et.al., 1962). These soils are represented by thin black Ah horizons overlain by either dark grey iron stained Bmg, or sandy loam Btj horizons. The pH ranges from approximately pH 7.2 in the Ah horizon to pH 7.7 in the C horizon. Free carbonates may be present in the lower Ah or Bm horizons.

2. Processing

As previously indicated, over 90 % of the current phosphoric acid is produced via the wet process. The wet phosphoric acid process involves the decomposition of phosphate raw materials (rock) with sulfuric acid. There are three basic wet processes presently used around the world. These include dihydrate, hemihydrate, and a hemi-dihydrate combination (Kouloheris, 1980). The differences between the three relate to the type of rock used, costs incurred, and quality of phosphoric acid produced. Briefly, the dihydrate process produces phosphoric acid with approximately 28 - 30 % P_2O_5 with the most impurities in both the acid and the waste gypsum. However, the ease of operation and flexibility in phosphate ore sources utilized make this process popular. Hemihydrate process produces acid which contains 40 - 48 % P_2O_5 with low levels of impurities. The costs of production are low but operation is limited by types of phosphate ores utilized, making this process less attractive. The hemi-dihydrate process again produces high quality strong acid (40 - 52 % P_2O_5) with pure waste gypsum. Difficulty in using certain rock sources and increased operating expertise make this process less popular.

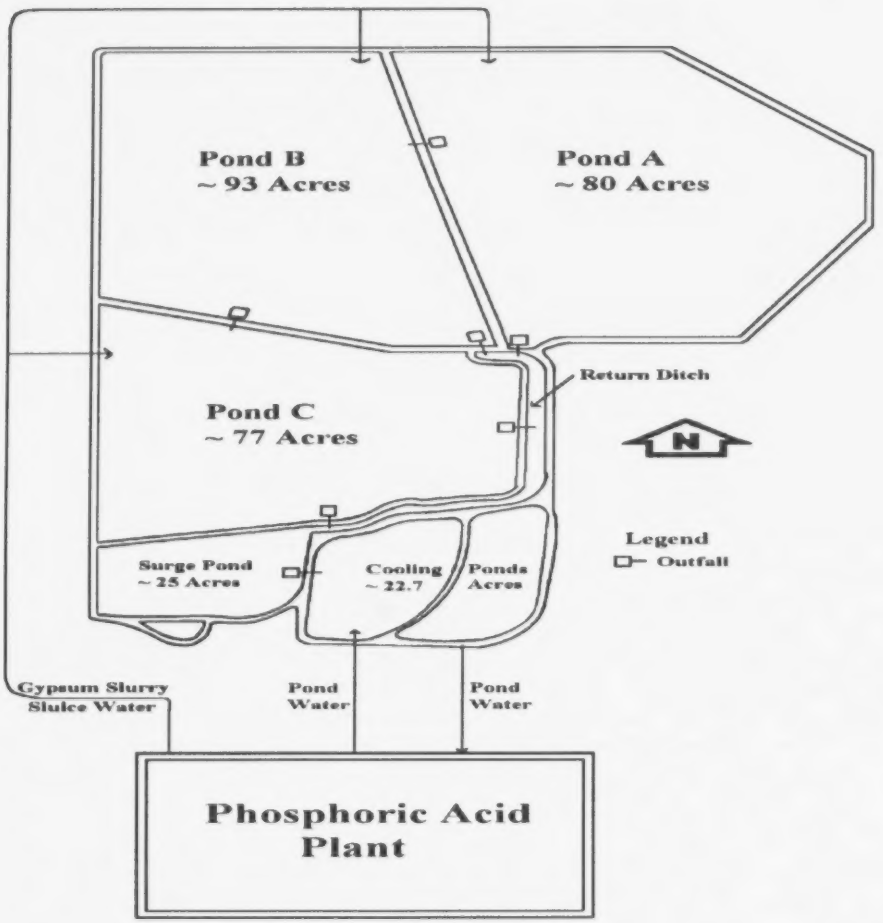


Figure 3. Plant site, Central Alberta, Canada..

The dihydrate process is most readily used throughout the world including the two operational sites in Alberta. The process, called Prayon Dihydrate involves various stages in order to attain the product P_2O_5. A phosphate rock grinding section is required in most cases although the plant studied utilizes Togo rock which does not need grinding due to the natural small particle size of this deposit which is acceptable for the dihydrate process (Becker, 1989). In the process phosphate rock, 93% sulfuric acid and water react in an attack tank in which the phosphate rock is decomposed into phosphoric acid and solid waste calcium sulfate dihydrate (phosphogypsum). The reaction is exothermic and thus requires cooling which is attained by cooling water.

The entire product is then filtered to separate the liquid P_2O_5 from the phosphogypsum waste. The filter section is one of the most important sections. It allows most of the P_2O_5 to be filtered off and in turn it removes the majority of the P_2O_5 from the phosphogypsum so there are less contaminants in the waste. The filtration is carried out in a series of four compartments (Fig. 4). The phosphoric acid slurry is pumped into the first chamber and the strongest P_2O_5 is filtered and directed to a storage tank. The filter cake then moves via conveyer belt into the next chamber for further washing. At each subsequent compartment further washing of the cake using lower and lower acid strength wash water is used until the final washing is done with the lowest P_2O_5 concentration. The washed phosphogypsum is then sluiced out of the plant using recycled wash water. The sluicing ratio is commonly 30% gypsum solids with 70% acidic process water.

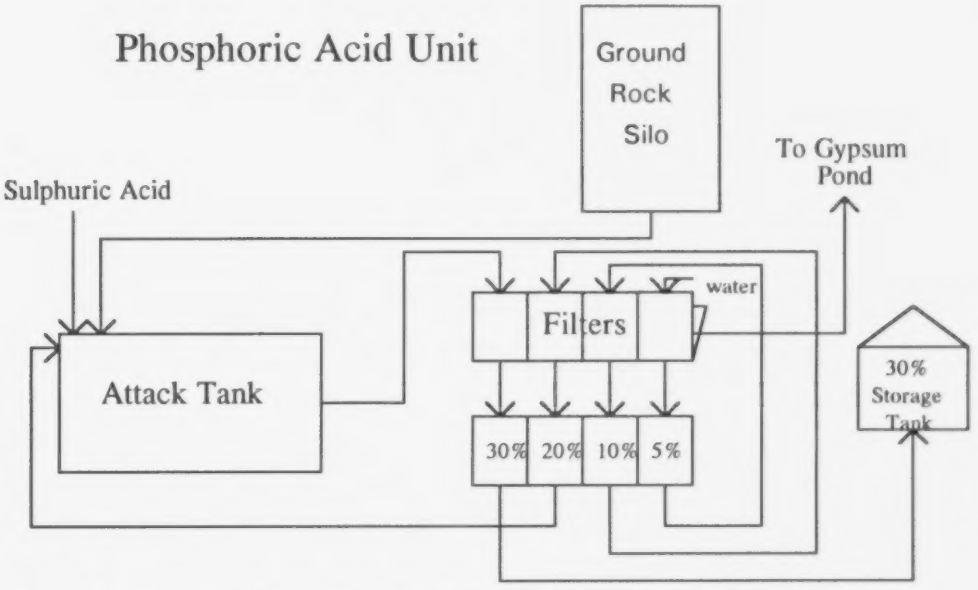


Figure 4. Phosphate plant filter diagram identifying route of phosphoric acid.

E. Waste Management

The sluiced material can either be wet stacked and stored or dumped into moving water bodies. The practice of dumping phosphogypsum into water bodies is no longer practiced in the U.S.A. due to a recent ruling by the U.S.E.P.A. which requires all phosphogypsum be placed in stacks or mines (Federal Register,

1990). There is still, however phosphoric acid plants around the world which dispose of their phosphogypsum wastes into rivers or oceans. Examples include the Djorf Lasfar plant in Morocco which pumps 25000 tons of phosphogypsum into the Atlantic Ocean per day (Becker, 1989). The Mediterranean, Adriatic, Baltic, and Black Seas are also areas of dumping. The North Sea receives phosphogypsum from the Elbe, Rhine, Seine, Thames, Humber, and Forth rivers from which phosphoric acid plants along these waterways freely disgorge their wastes. The Irish Sea receives approximately 75000 tons of phosphogypsum per year from Belfast, Whitehaven, and Avenmouth and may be the most radioactive polluted sea in the world (Ferguson, 1988). One thing which must be noted is that in most instances where dumping into water courses occurs, the level of contaminants in the sluiced material is much less than those found in recycled sluice material (McBeath, 1987). There are environmental concerns regarding dumping into aquatic environments and thus the second option, wet stacking, may be the only alternative.

The majority of the phosphogypsum produced world wide is wet stacked. This involves sluicing the the phosphogypsum and acidic process water via pipes into impoundment ponds. Approximately 4.5 - 5.5 tons of phosphogypsum are produced for each ton of P_2O_5 (Ferguson, 1988). The purpose of the phosphogypsum stack and tailings pond is to provide storage for the solid wastes and act as settling ponds in which the liquid sluice water is channeled into cooling ponds so the water can be recycled back to the plant. At the studied plant all contaminated effluent from the plant is recycled to the gypsum pond (McBeath, 1987). The stacks are designed for settling of the crystallized phosphogypsum and allow the process water to be directed to a cooling pond using perimeter dykes and drains. Any water that may seep or leach through the stack is again routed via drains to the cooling pond so there is essentially complete recycling or a closed loop. There are monitoring wells placed around the pond and dry stacks to check for seepage of effluent to the groundwater (McBeath, 1987).

1. Management to Prevent Groundwater Contamination

Environmental considerations bring forth intensive management towards both phosphogypsum stack and sluice water cooling pond management. As previously indicated the most popular method of disposing of the phosphogypsum is through wet stacking. The most negative environmental impact from this type

of operation is contamination of the groundwater in the stack vicinity and movement of contaminants within the groundwater regime. The sluice water found in the gypsum pores and in the cooling pond is highly acidic and contains high levels of environmentally sensitive elements (Wissa and Fuleihan, 1980). There are therefore generic concerns regarding (1) contamination of groundwater at active stacks by leaching sluice water and (2) long term contamination by infiltrating rainwater after stack closure (SENES, 1987). To overcome and monitor these possible scenarios various techniques are utilized by industry to maintain a completely closed system and prevent migration of contaminants off site. These techniques take into consideration that there may be movement either by surface runoff and/or percolation.

2. Prevention of Surface Runoff

Surface runoff of sluice water from both the phosphogypsum stack and/or cooling pond are situations which must be examined and proper engineering practices must be undertaken for prevention. Adequate water containment is important. Most phosphate plants utilize dyke methods to contain the sluiced material. These dykes are made up of the phosphogypsum tailings and can be arranged by two methods. Ring dyke impoundment, used at Western Co-operatives Fertilizer Ltd. in Calgary and Esso Chemicals in Redwater, involve using the phosphogypsum on all sides of the pond. This method is best adapted to flat terrain whereas the second method, valley dyke, is used where the existing topography encloses a portion of the pond (Norlander, 1988). Valley dyke method of impoundment is used at Western Co-operatives Fertilizers Ltd. in Medicine Hat and Sherritt Gordon in Fort Saskatchewan. Using these methods of impoundment results in no waste water leaving the plant site. One exception may be if the rainfall in that area is high enough to exceed evaporation and there is periodic overflow. In this case the overflow pond water must be neutralized by a two stage calcium carbonate, lime treatment until pH 8.8 is achieved and the levels of contaminants are low (Becker, 1989). Most surface runoff is directed via return ditches to cooling ponds so there is less opportunity for the sluice water to run off site.

There has been some instability noted for the phosphogypsum dykes in the Alberta phosphate plants. Esso Chemicals has had one interior dyke fail due to ice lense formation (Conlin, 1984). Sherritt Gordon has also had some failure and

replaced a section of the dyke (Norlander, 1988). Thus the potential for contamination is still present.

3. Leaching

A situation more likely to occur at phosphogypsum stacks and cooling ponds is for the sluice water to leach through the gypsum pore spaces and to enter the subsurface environment. Phosphogypsum is quite porous (up to 50% porosity) and contains large amounts of sulfuric, phosphoric, and hydrofluoric acids. Along with these acids are radionuclides and trace elements solubilized from phosphate rock during the phosphoric acid processing. To prevent this acidic sluice water from entering groundwater a number of managerial methods can be employed. These include the use of drainage pipes, interceptor wells and ditches, synthetic or clay liners, and calcareous materials.

4. Use of Drains, Ditches and Interceptor Wells

Most currently operating phosphogypsum stacks observe leachates percolating downward and laterally towards the subsurface groundwater. The use of drain systems under and around the base of the stack serve to collect the leachate and prevent groundwater contamination (Berish, 1990; Becker, 1989; and Wissa and Fuleihan, 1980). Drains can also be in the form of interceptor wells. The water level in these wells are maintained below the groundwater level by pumping. The pumped leachate is returned to the cooling pond for recycle. Maintaining wells lower than the groundwater serves to collect all seepage that eludes liners and ditches (Berish, 1990 and Becker, 1989). The use of drains and ditches aids in removing percolating sluice water but the maximum protection against environmental contamination is attained by a combination of drains and impervious vertical and horizontal barriers.

5. Use of Liners

Restrictive barriers can be engineered synthetic or clay liners or impervious natural subsurface earthly material. The use of synthetic liners, polyethylene foil, hypalon (Becker, 1989) may have limitations due to deterioration by the chemically aggressive acidic sluice water. The liners must also be able to overcome weathering effects and depending on the stack location, climatic changes. In areas where appropriate soils for liners cannot be found and

inappropriate subsurface conditions prevail, the use of synthetic liners may be the only alternative. This is especially true for stacks close to public water supplies as noted by Wissa and Fuleihan (1980). Sherritt Gordon in Fort Saskatchewan found it necessary to use a polyethylene liner for their phosphogypsum pond which is located on highly permeable subsurface geologic materials (Norlander, 1988).

A more economic approach is to use clay liners. Clays exhibit natural tightening properties which form impermeable layers. The tightening properties of soil relate to their components, iron and aluminum silicates, and carbonate containing materials. Upon reaction with acidic pond water these components form Fe and Al- phosphates, Ca-phosphates, Ca-fluorides, and amorphous silica, all which have tightening properties (Becker, 1989). Clays are also electrically charged and thus participate in sorption reactions. Clays can either be positively of negatively charged depending on soil pH and have the ability to attract and attenuate mobile, environmentally sensitive ions found in the leaching sluice water.

Again, as with synthetic liners, clay liners are usually used in conjunction with seepage collection measures. The clay liners must also be implemented properly to avoid the formation of damaging cracks and crevices which reduce the effectiveness of the liner. The use of clay as an effective attenuator of environmentally sensitive radionuclides, heavy metals, and trace elements in the phosphogypsum sluice water is one aspect examined in this research. Also examined is the attenuation as a result of sluice water neutralization.

6. Neutralization as Control

Neutralization of sluice water and phosphogypsum leachate is one measure of groundwater protection which is used worldwide. As indicated the leaching sluice water is very acidic (pH $<$ 2.0) and typically contains high levels of contaminants, some reaching equilibrium concentrations (McBeath, 1987). These acidic seepage waters may be buffered by alkaline subsoils and calcareous layers thereby reducing the mobility of certain heavy metals (SENES, 1987). The calcareous nature performs a "purifying" process on the leachate. Soluble contaminants in acid solution form insoluble stable precipitates when neutralized. Certain elements, F, PO_4 (Wissa and Fuleihan, 1980; Muthukumar and Subrahamangam, 1987; and McBeath, 1987), Ni, Co, Cu (SENES, 1987) have

been found to decrease greatly in concentration due to neutralization with carbonate minerals. Neutralization, therefore, is one possible method of environmental control for phosphogypsum waste disposal (Wrench and Smith, 1986).

F. Elements of Concern

Table 3. Chemical characteristics of sluice water and selected drinking water guidelines (mg/L).

Elements	Sluice Water Values	Canadian Maximum Allowable Concentration	U.S. Maximum Contaminant Level	E.P.A. Effuent Maximum Contaminant Concentration
As	1.3	0.05	0.05	5.0
Cd	2.0	0.005	0.01	1.0
Cr	1.8	0.05		5.0
Cu	1.1			
F	4700	1.5	4.0	
Hg	n/a	0.001		0.2
Mn	5.5	0.05	0.05	
Ni	187			
Pb	0.3	0.01	0.05	5.0
PO_4				
Se	0.7	0.01	0.01	1.0
SO_4	8600	< 500	250	
U	3.5	0.02	n/a	
Zn	5-7	< 5.0		
pH	1.6	6.5 - 8.5	6.5 8.5	
TDS	n/a	500	500	
Ra-226	1.9 - 3.2 Bq/L*	1.0 Bq/L	0.19 Bq/L	
U-238	60 Bq/L			

n/a values not available

* Miller and Sutcliffe Jr. (1982)

The phosphogypsum sluice water is highly acidic and contains high levels of sulfates, phosphates, fluoride, total dissolved solids, radionuclides, heavy metals, rare earth elements, and some trace elements. These chemical species are the result of unreacted feedstocks, phosphate rock and sulfuric acid, and the

products of chemical reaction. Many of these elements are soluble and partition into the sluice water and thus will be mobile upon deposition at waste sites. Table 3 illustrates many of these elements of importance with respect to their concentrations in sluice water in comparison with drinking water guidelines. The table shows that the sluice water exceeds drinking water guidelines for all constituents listed. There is concern related to the release of these contaminants into soil and aquatic environments.

1. Major Elements

Fluoride

The concentration of fluoride in sluice water is sufficiently high to be considered toxic. Table 3 shows the Canadian and U.S. drinking water guidelines for F^- at 1.5 and 4.0 mg L^{-1}, respectively. The sluice water in this study has a concentration of approximately 3.5 orders of magnitude greater. Fluoride is therefore of great concern.

Fluoride is the 12th most abundant element in igneous rock and the 3rd most abundant anion (Bar-Yosef, et.al., 1989). Fluoride is present in the phosphate rock utilized in the phosphoric acid industry. Much of the fluoride ends up as fluorine exhaust gasses from digesters and crystallizers. Scrubbers are used to remove the fluorine gasses and thus convert the environmental problem from air emission problems to potential leachate problems. The scrubber wastes enter the waste stream and eventually become a part of the sluice water. The fluoride is present in the waste water as fluorosilicic acid (H_2SiF_6)(aq), hydrofluoric acid (HF)(aq), and silicon tetrafluoride (SiF_4)(aq) (Muthukumar and Subramanyam, 1987).

The environmental problems associated with fluoride include detrimental effects on both plants and animals. In minor amounts fluoride is beneficial but in high amounts (30-50 mg L^{-1}) is considered toxic (Underwood, 1971). Plant symptoms of excess F include reduced yields due to altered enzyme activity (Yang and Miller, 1963) and reduced cellular Ca and Mg (Cook, et.al., 1976). Fluoride, at differing levels of toxicity have different effects on mammals. At less than 2.4 mg F^- L^{-1} dental fluorosis can occur while crippling fluorosis can occur at an intake of 20 mg/day and death at 2250 - 4500 mg L^{-1} in a single dose

(Murray and Lewis, 1985). Excess fluoride in mammals is also known to cause bone cancer (Bohn, et.al., 1985), chromosome aberration and unscheduled DNA synthesis (Tsutsui, et.al., 1984).

Fluoride leaching and transport in the saturated zone has been studied in the past and studies have shown that there is reason for concern. Rouis and Bensalah (1990) found in their study that fluoride migrated both downstream and laterally from a phosphogypsum stack. Even at 1000 m downstream and 300 m laterally the fluoride concentration was 10-40 mg L^{-1}. Such concentrations are generally considered unsuitable within aquifers.

2. Radionuclides

During the wet phosphoric acid process radioactivity equilibrium within the phosphate rock is disrupted and the radionuclides are partitioned into various phases according to their solubility (Lardinoye, et.al., 1982, and Roessler, et.al., 1979). Uranium, thorium, and lead distribute primarily into the liquid phase while radium and polonium partition into the solid phosphogypsum (McBeath, 1987 and Berish, 1990). Roessler et.al. (1979) determined that 90% of the uranium passes into the phosphoric acid and about 90% of the radium goes into the phosphogypsum (Fig. 6).

i. Uranium

Residual phosphoric acid within the phosphogypsum pores may contain dissolved U at levels which may be of environmental concern. Uranium occurs as U-234, U-235, and U-238 isotopes with relative abundances of 0.0056%, 0.72%, and 99.27% respectively (Ames and Rai, 1978). Uranium-238 is the radionuclide of greatest environmental consideration. Studies have shown increased concentration of U-238 chain radionuclides in aquatic environments at phosphogypsum disposal sites (Koster, et.al., 1985, and Kobal, et.al., 1990). Uranium exists mainly in the stable +4 and +6 oxidation states. In oxidizing conditions, which is expected to be found within gypsum stacks, uranium remains in a soluble form. The oxidized form, U +6, is quite soluble and mobile. At pH less than 5, uranyl (UO_2^{+2}) ions and uranyl fluoride dominates. As pH increases to 7.5, $UO_2(HPO_4)_2^{+2}$ occurs and at even higher pH uranyl di- and tri-carbonate species occur. The most soluble forms of uranyl minerals occur at pH less than 5,

thus, they occur in the sluice water (Rutherford, et.al., 1994). The reduced form of uranium , U +4, is less mobile and insoluble. Uranium (IV) can substitute for Ca^{+2} and at low pH form complexes with fluoride. The maximum allowable concentration (MAC) of uranium in Canadian drinking water is 0.1 mg L^{-1} although no MAC for U-238 is reported (Federal - Provincial Subcommittee on Drinking Water, 1989).

ii. Thorium

Traces of Th-228 and Th-230 have been found in groundwaters although the levels are quite low as compared to other radionuclides. The element forms soluble compounds with hydroxides, fluorides, phosphates, sulfates, nitrates, and chlorides. Thorium is most mobile at pH < 5 (Ames and Rai, 1978).

iii. Lead

Lead - 210 partitions into the liquid phase and has the potential to migrate into groundwaters. Concentrations may be kept low due to formation of insoluble lead carbonate and $PbSO_4$ (s) in oxidizing environments and as PbS (s) under reduced conditions (Upchurch, et.al., 1991).

iv. Radium

As indicated most Ra-226 is partitioned into the solid phosphogypsum, thus the threat for groundwater contamination will only be warranted if radium dissolves and forms soluble mobile compounds. SENES Consultants Ltd. (1987) have found instances where high levels of Ra-226 have been found in groundwater. This may be due to the formation of soluble $RaSO_4^o$ and $RaCO_3^o$ complexes (Upchurch, et.al., 1991). Studies have also shown that groundwater conditions of high ionic strength with high concentrations of competing ions may out-compete Ra-226 for adsorption sites and allow Ra-226 to remain in solution (Kaufman and Bliss, 1977). The main concern of Ra-226 is its eventual decay to radon. Radon-222 is an alpha emitter and quite soluble. If ingested or inhaled this radionuclide and its decay products can be quite harmful, contributing to lung cancer (Berish, 1990).

3. Trace Elements

Elements classified as toxic by EPA standards include As, Ba, Cd, Cr, Pb, Hg, Se, and Ag (Federal Register, 1980). As seen in Table 3 many of these elements are increased in concentration over drinking water guidelines. Major elemental concerns are aimed at those elements which are solubilized during the wet process phosphoric acid production. These include As, Cd, Cr, Fe, Se, and U (Becker, 1989 and Berish, 1990).

i. Arsenic

Arsenic is an element of consideration due to its toxicity towards plants and animals. Arsenic competes with important plant metabolites for adsorption sites (O'Neill, 1990). Although plant uptake is low, arsenic partakes in the occupation of sites for essential groups. Arsenic compounds are used as pesticides.

ii. Cadmium

Cadmium has no essential biological function and is highly toxic to plants and animals. Cadmium reacts with plant cell membrane which effects its permeability (Alloway, 1990). Because of its toxicity, several countries have restricted the use of cadmium.

The inherent problem with cadmium is that it is toxic to nearly all living organisms and consequently its concentration in the environment is of great concern. The kidney is the critical organ of intoxication after long-term exposure to cadmium (Hutton, 1987). Renal dysfunction is in the form of increased urinary excretions of high molecular weight proteins. Cadmium has also been associated with hypertension (Schroeder, 1965), emphysema, and chronic bronchitis (Lewis, et.al., 1969). Another health concern of cadmium involves its substitution with calcium in the bones. 'Itai-itai disease' in Japan during the 1960's was a severe cadmium caused disease (Hutton, 1987). These were the first health effects reported to populations outside of those which involved direct occupational exposure to cadmium. Many areas of Japan are contaminated with cadmium as a result of discharges from numerous non-ferrous metal mines and smelters (Hutton, 1987). Long-term consumption of rice grown in these areas resulted in the

outbreak of the disease. There are numerous pathways in which cadmium can enter the food chain and the human body.

Plants and animals can absorb cadmium from the soil and atmosphere and accumulate it in their bodies. Cadmium in soil solution can behave as calcium and be taken up by plants. The health risk of cadmium contamination increases as its entry into the food chain expands. Cadmium toxicity hence can reach humans through the uptake by plants as well as groundwater contamination and because of this, determination of the distribution of cadmium among various chemical forms in the soil solution is important in ascertaining its bioavaliability. To correctly identify the extent of pollution and predict the potential harm caused by Cd in the soil and water system we must positively identify its fate in the system. Knowledge of the soil chemistry of Cd is necessary for evaluating the consequences of continued addition of Cd to soils.

iii. Chromium

Chromium can be toxic to plants, animals, and humans (Bartlett and Kimble, 1976a). The hexavalent form of chromium is the most toxic and the most mobile in the environment and can cause the greatest negative environmental impact (Bartlett and Kimble, 1976b). Chromium (III) is less toxic but is still of concern if disposed of in landfills or waste repositories, due to its ability to be oxidized to Cr (VI) (Bartlett and James, 1979).

iv. Selenium

Selenium is a highly toxic element to plants, animals, and humans. Selenium competes for sites with metabolites and essential ions (major cations) in its effects on plants (Neal, 1990). Plants growing on selenium toxic areas incur 'selenosis' causing chlorosis of leaves and pink coloration of roots. Selenium is also toxic to animals. Selenium is an essential element but can be toxic to animals in excess amounts. There is a narrow range between deficiency at a minimum of 0.1 ppm and toxicity at 3 - 4 ppm in feed (Neal, 1990). Insufficiencies can result in 'white muscle disease' in livestock while toxicity's can cause 'blind staggers' and 'alkali disease' in cattle and may result in death in cattle and sheep.

G. Summary

The previous discussion provides an overview of the phosphate fertilizer industry and the environmental problems that may be associated with waste disposal. In Alberta there are presently four phosphogypsum sites which contain vast amounts of stored phosphogypsum. These four plant sites all used or presently use sluicing techniques as previously discussed in the literature review. The potential environmental problems are therefore similar for all sites.

The composition of the sluice water is such that concern is warranted over the proper safety procedures used for storage and handling. The composition with regards to major, minor, and trace elements as well as radionuclides warrants further study as to determine potential adverse effect on soil and water quality. Engineered controls are being used at all sites to ensure minimal migration of possible contaminants but even with such controls some sluice water may enter the subsurface environment. At all locations, calcareous geological material (till, alluvian, and weathered shale) underlies the waste repositories. It is logical to expect that attenuation of constituents dissolved in sluice water occur upon reaction with calcareous subsoils. The extent of precipitation and adsorption of environmentally sensitive elements in the phosphogypsum sluice water has however, barely been studied. Therefore, this study examines attenuation by chemical neutralization of acidic sluice water and by adsorption on soil clays.

CHAPTER III

MATERIALS AND METHODS

A: Phosphogypsum Sluice Water

1. Sampling

Phosphogypsum slurry samples were collected from an exit valve on route to the gypsum settling stack and cooling ponds at an active phosphoric acid processing plant at Redwater, Alberta. Two separate samples were collected approximately one month apart to ensure consistent characteristics of slurry mixture. Both samples have nearly identical pH and solids content. The slurry samples were collected in 22.7 L (5 gallon) plastic buckets and sealed with snap-on lids. A total of 9 buckets were collected. The samples were greyish in color and at a temperature of 70 - 80 ^{o}C at the time of collection.

2. Material Treatment

Upon returning to the laboratory the samples were stored at 5 ^{o}C prior to filtration. All samples were separated into liquid and solid phase. Initial separation consisted of pouring off the supernatant from which the solid phosphogypsum had settled. The solution was then filtered twice under vacuum using a buchner funnel and Whatman #42 filter paper with an approximate pore diameter of 2.5 um. The samples from each individual sampling date were analyzed for pH and electrical conductivity (E.C.) to ensure similarity in composition. The two sluice water samples were then blended into one composite sample and stored at 5 ^{o}C. The samples were pale yellow in color.

3. Initial Analysis

Hydrogen ion activity (pH) was determined using a Corning model 10 pH meter and a standard polymer body gel-filled combination electrode. Electrical conductivity was measured using a Model 31 Conductivity Bridge and the method proposed by Bower and Wilcox (1965).

B. Soil

1. Sampling

One bulk sample from the Bt horizon of an Orthic Grey Luvisol was collected from Ardrossan, Alberta, (NW Sec 14, Twp 52, Rge 23, W4). The soil is classified as the Cooking Lake Loam (soil series). The bulk sample was collected in a 22.7 L (5 gallon) plastic bucket and sealed with a snap-on lid.

2. Material Treatment

In the laboratory the soil sample was spread out on paper and air dried for one week. The soil was then crushed using a hammer mill followed by grinding in a roller mill until the soil was < 2mm in diameter. The sample was then blended and stored.

3. Initial Analysis

Hydrogen ion activity (pH) was determined in 0.01 M $CaCl_2$ using the technique of Peech (1965). Three replicate measurements were carried out. Detailed soil analysis were previously conducted by Abder-Ruhman (1980). Table 4 shows a complete summary of soil chemical and physical properties. Mineralogy analysis was also performed by Abder-Ruhman (1980) and are presented in Table 5.

The soil description as provided by Abder-Ruhman (1980) is as follows:

Horizon	Description
Bt	40-65 cm; dark brown (10 YR 4/2m.); sandy clay loam; strong fine to medium subangular blocky; firm; few medium random and few fine vertical imped and exped roots; few fine clay skins; gradual smooth boundary; 23 -28 cm thick.

Table 4. Chemical and physical soil properties of the Bt horizon.

PROPERTY	QUANTITY
pH in distilled water	6.5
pH in 0.01 M $CaCl_2$	6.0
Organic Matter %	0.96
$CaCO_3$ equivalent %	0.00
Exchangeable Cations (me/100g)	
Al^{+3} plus H^+	1.43
Na^+	0.09
K^+	0.21
Ca^{+2}	13.51
Mg^{+2}	6.36
C.E.C. me/100g	21.60
Particle Size Analysis	
course and medium sand %	16.8
fine sand %	29.2
course silt %	8.3
medium silt %	8.7
fine silt %	3.4
course clay %	12.4
fine clay %	21.2

Table adapted from Abder-Ruhman, (1980).

Table 5. Physical, elemental, and mineralogical analysis of clay fraction (Bt horizon) used in adsorption experiments.

PROPERTY	QUANTITY
Physical and Elemental analysis	
C.E.C. Ca exchange capacity me/100g	58.4
C.E.C. K exchange capacity me/100g	42.8
Surface Area m^2/g	423
Na_2O %	0.36
K_2O %	2.01
CaO %	0.09
MgO %	2.33
Fe_2O_3 %	9.71
Mineralogical analysis	
Organic Matter %	not detected
Carbonates %	0
Mica %	20
Vermiculite %	10
Smectite %	40
Kaolinite %	25
Quartz %	4
Chlorite %	1
Feldspars %	0

Table adapted from Abder-Ruhman, (1980).

C. Experimental Set-Up

1. Chemical Neutralization

The first experiment was conducted to determine how concentrations of soluble constituents in phosphogypsum sluice water changed upon neutralization with a base. The purpose of these experiments are to identify how chemical precipitation contributes to attenuation. The experimental procedure represents a step by step neutralization of the acidic sluice water in order to identify solubility-pH relations of elements of concern. These experiments are intended to simulate leaching phosphogypsum pore water through a calcareous environment and the subsequent neutralization by reaction with carbonate minerals. Ion activities calculated from elemental concentrations at or near equilibrium at each pH point

along the neutralization curve are then used to predict solubility controlling solids that may be present.

A set of batch incubations were designed to obtain a wide pH range of phosphogypsum sluice samples. Incubators consisted of 750 ml polyethylene containers with snap-on lids. Each lid contained a central 1 cm circular opening to allow ease of pH measurements and to maintain aerobic conditions within the incubator. The study incorporated different pH treatments in triplicate. The average treatment pH values were 1.6, 2.3, 3.6, 4.7, 5.4, 6.2, 7.3, 7.8, 8.7, and 9.7. Calcium hydroxide powder was used to achieve the desired pH (Fig. 5). Initially $CaCO_3$ (s) was to be used in the experiment but difficulty arose in reaching the higher pH values while maintaining a usable solution. Preliminary experiments showed that using $CaCO_3$ for neutralization resulted in the formation of a paste and excess frothing followed by solution solidification. Calcium hydroxide was chosen as the neutralizing agent to maintain the high calcium concentrations in the sluice solution and to achieve the desired pH.

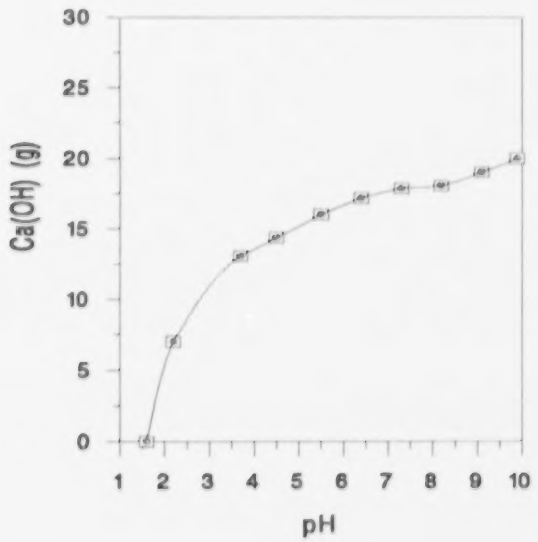


Figure 5. Amounts of $Ca(OH)_2$ vs. pH value of sluice water.

Seven hundred millilitres of sluice water was added to each batch container followed by additions of $Ca(OH)_2$ (s) (Fig. 5). All samples were done as two sets

of triplicate; one set for the precipitation experiment and one set for the adsorption experiment. The batch containers were stirred on magnetic stirrers for 1 hour to ensure pH stabilization. Throughout this period pH was measured using a combination electrode. Upon pH stabilization the individual treatments were centrifuged at 10400 G's for 15 minutes at 10 - 20 ^{o}C. The supernatant was poured back into the 750 ml incubation containers and the pH checked. The batch vessels were allowed to sit for a period of 2 weeks over which time pH was recorded. In solubility equilibrium studies reliable samples can only be obtained after the chemical system reaches a steady state (Zachara and Streile, 1990). Following the 2 week incubation period the treatments were again centrifuged at 10400 G's for 15 minutes to remove all suspended and precipitated material. The supernatant was then stored in polyethylene containers at 5 ^{o}C prior to analysis.

2. Soil Adsorption

The second experiment was designed to determine the contribution of adsorption to the attenuation of dissolved constituents in phosphogypsum sluice water when it reacts with soil clays. Batch incubation of the pH altered sluice water with an Orthic Gray Luvisol Bt horizon soil was performed. The sluice water and soil was mixed at a 10:1, liquid:solid ratio. The batch technique employs a small solid to liquid ratio and therefore is representative of waste leaching in a ponded environment (Environment Canada, 1990). The incubators used are the same 750 ml containers used in the first phase. The soil - sluice solutions were mixed 2 times per day over a 14 day period using a milkshake mixer. The ambient temperature and pressure of 21 -23 ^{o}C and 1 atmosphere respectively were maintained throughout the incubation. Solution pH was monitored and recorded over the incubation period. Following the 2 weeks the solutions were centrifuged for 15 minutes at 10400 G's and then the supernatant was filtered through Whatmans #42 filter paper to remove any organic debris (root fragments). The samples were stored at 5 ^{o}C for analysis.

3. Evaporation Experiment

The soil adsorption experiment involves a two week longer time period and more extensive agitation than the chemical neutralization experiment and thus the samples are susceptible to increased evaporation. Evaporation of liquid from the sluice water treatments tends to increase the concentration of some dissolved

constituents. A correction factor must then be implemented in order to compare concentrations to the first experiment. To determine the correction factor a blank sluice water sample of 650 ml was put through the same experimental procedure as the adsorption phase. Evaporation was measured as the difference between the initial and final volume of sluice water following the 14 day equilibration period. It was found that approximately 34 ml of sluice water evaporated. This amount was calculated as a percentage of the total volume of sluice used in each treatment.

The following example illustrates the calculation:

34 ml evaporated / 667 ml sluice averaged @ pH 1.6
The correction factor (CF) @ pH 1.6 is 34/667 = 5.1%

Table 6 shows the correction factors for each treatment pH. To determine the actual concentration using the correction factor the following calculations must be made:

we know the [original] + [CF%]
let Y = [original]
$Y + (CF\%)(Y) = [total]$
$Y(1 + CF\%) = [total]$
$Y = [total] / (1 + CF\%)$

An example: @ pH 1.6 and $[M^{+2}] = 4$ mg L^{-1}
$Y = 4 mg\ L^{-1} / (1 + 0.051)$
$Y = 3.8$ mg L^{-1}

The reported concentration of element M^{+2} would be 3.8 mg L^{-1} rather than 4.0 mg L^{-1}.

Table 6. Correction factors (CF) for adsorption experiment as a result of evaporation.

Treatment pH	Correction Factor %
1.6	5.1
2.4	5.4
3.6	5.4
4.7	5.9
5.5	6.2
6.5	5.8
7.3	5.7
7.9	5.7
9.0	5.7
9.9	5.8

D. Analysis

1. Gamma-Emitting Radionuclides

All treatment samples for the neutralization and adsorption experiment were analyzed for gamma-emitting radionuclides. Sluice water supernatant from each treatment (450 ml) was placed into 500 ml Marinelli beakers and lids sealed with a silicon caulking compound to ensure an air tight container. Samples were analyzed for radionuclides using a gamma spectrometer following a 125 day ingrowth period. Not all members of the U-238 decay series can be determined directly by γ-spectrometry, however, if sufficient time elapses between the last time the sample was sealed and the time of measurement, decay daughter products will be in secular equilibrium with the hard to measure long-lived nuclides of interest. The required time is 5 times the half-life of the daughter nuclide (Abel, 1986). In order to measure U-238 from Th-234 we require 5 times the half-life of Th-234 (24.1 days), a period of 125 days. A blank utilizing distilled deionized water (450 ml) was also sealed for 125 days and analyzed for background level radionuclides.

The gamma spectrometer used consisted of a 42% hyperpure Ge semiconductor detector, contained within a lead castle, connected to an Aptec ™ multichannel (8192 channels) analyzer. Data was collected and analyzed with Aptec PCMCA/WIN ™ software. Calibration involved a sealed Amersham ™

gamma source containing Cd-109, Co-57, Ce-139, Hg-203, Sn-113, Sr-85, Cs-137, Y-88, and Co-60 as chlorides, incorporated into a 450 ml solid plastic matrix found within a geometrically similar Marinelli beaker as those used for sample analysis. Calibration was checked using CANMET ™ UTS-1 uranium tailings (450 ml) placed into a 500 ml Marinelli beaker. Treatment and blanks were counted for 48 hours (172800 seconds) to improve counting efficiencies and reduce % error.

The specific activity of U-238 in the phosphogypsum sluice water samples was determined by measuring the Th-234 activity at 62 and/or 93 keV. The reported activities at 93 keV is actually a sum of two close energy peaks. The actual activity was found by dividing the value at 93 keV by 2. Activity is reported at 93 keV due to improved counting statistics than that at 62 keV. Similarly, the specific activity of Ra-226 was determined by measuring Pb-214 at 295 and 352 keV, and Bi-214 at 1120 and 1764 keV.

2. Chemical Analysis

Treatment samples from the neutralization-precipitation and the adsorption experiments were analyzed for 21 major, minor, and trace elements. Major elements, Ca, Mg, Na, K, and P and trace elements, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, U, V, and Zn were analyzed using Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP) at an external laboratory[1]. Detection limits for these elements are listed in table 7.

Determination of total arsenic involved the digestion of sluice water treatment samples in concentrated HCl and generation of arsine gas using the method of Melton, et. al. (1973). The arsine gas was collected in an iodine solution and arsenic was quantitatively measured colormetrically by the molybdenum - blue method of Small and McCants (1961).

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Table 7. Table of elemental analysis techniques and detection limits.

CONTAMINANT	ANALYSIS TECHNIQUE	DETECTION LIMIT ug L^{-1}
As	colorimetry	1
Ca	ICP	1
Cd	ICP	9
Co	ICP	9
Cr	ICP	9
Cu	ICP	3
F	electrode	500
Fe	ICP	3
K	ICP	300
Mg	ICP	1
Mn	ICP	3
Na	ICP	30
Ni	ICP	9
P	ICP	60
Pb	ICP	60
Se	ICP	60
SO4	turbidimetrically	1
U	ICP	60
U-238	gamma-spectroscopy	3 Bq L-1
V	ICP	3
Zn	ICP	9

Sulfate was quantitatively determined turbidimetrically using the Standard Methods for examination of Water and Waste Water 16th Edition (1985). The procedure has been slightly modified in that Sulfa. Ver IV powder pillows were substituted for barium chloride.

Total fluoride was measured using a Orion combination fluoride ion-specific electrode and analyzed on a Orion microprocessor ionanalyzer/901. The electrode is sensitive to the free fluoride ions between pH 5-8. The solutions were first treated with TISAB buffer in order to dissociate fluoride complexes and to stabilize pH (Standard Methods for examination of Water and Waste Water 16th Edition, 1985). Concentration curves were constructed with standard KF solutions and these were used to calibrate the electrode.

3. Routine Analysis

Throughout the experiments and for each treatment sample, pH and EC were determined as reported previously.

4. Computer Modeling

All data collected from the batch incubations on chemical neutralization and soil adsorption were used to calculate the activities of ionic species present in solution. GEOCHEM-PC version 2.0 (Parker, et. al., 1990), a modified version of GEOCHEM (Sposito and Mattigod, 1980) which is a geochemical equilibrium based thermodynamic computer model was used to calculate speciation and ion activities within the solutions. This allows us to relate ion activities to theoretical levels determined from solubility constants for candidate solubility controlling solids which may be present. Saturation indices with respect to solubility controlling solids can then be determined to identify the presence of solubility controlling solids.

Input parameters include pH, Ionic Strength (I) as (mol L^{-1}), and analytical concentrations of anions and cations present. Ionic Strength is calculated from measured EC values, (= 0.013 EC (dS m^{-1})) (Griffin and Jurinak, 1973). Ionic Strength is entered as an estimate and the program itself calculates I from speciated levels of each ion. Likewise alkalinity is calculated from an assumed atmospheric CO_2 partial pressure of $10^{-3.5}$ bars (Bohn, et. al., 1985). Elements are entered into the program in the form they are expected to be found in solution. Calcium is entered as Ca^{+2}, Mg as Mg^{+2}, K as K^{+}, Na as Na^{+}, Fe as Fe^{+3}, Mn as Mn^{+2}, Cu as Cu^{+2}, Cd as Cd^{+2}, Zn as Zn^{+2}, Ni as Ni^{+2}, Cr as Cr^{+2}, U as UO_2^{+2}, S as SO_4^{-2}, F as F-, P as PO_4^{-3}, As as AsO_4^{-3}, and Se as SeO_4^{-2}.

CHAPTER IV

RESULTS AND DISCUSSION

A. Initial Analysis

Table 3 (shown earlier) illustrates some of the more crucial environmentally sensitive elements which are found within the sluice material. These concentrations (Table 3) are shown with respect to both maximum effluent concentration guidelines and Canadian and U.S. drinking water guidelines. A number of elements are elevated with respect to these guidelines and thus concern is raised if these elements enter the groundwater and remain in soluble form presenting danger to plants, animals, and humans. The main characteristics of sluice water of interest which will be discussed in further detail are: pH, sulfate, fluoride, radionuclide U-238, and the trace elements arsenic, cadmium, chromium, and selenium.

1. pH

Results of the initial characterization indicate that the pH of the sluice water exiting the phosphoric acid plant into the gypsum and cooling pond is around pH 1.6. This value is very acidic and therefore the sluice water is expected to contain high levels of soluble components. Both Canadian and U.S. drinking water guidelines indicate that pH in the range of 6.5 to 8.5 is acceptable (van der Leeden, et.al., 1990). The pH of the sluice water is much lower than the acceptable pH and is therefore of potential concern.

2. Electrical Conductivity

The electrical conductivity (E.C.) measured at the time of effluent discharge is 23 dS m^{-1} . This value indicates high levels of soluble salts or dissolved constituents. By use of simple conversion we can predict ionic strength (I), salt concentration ([salt]), and osmotic pressure using the following relationships:

$$I \text{ (mol } L^{-1}) = 0.013 * \text{E.C.}$$

$$[\text{salt}] \text{ (mg } L^{-1}) = 640 * \text{E.C.}$$

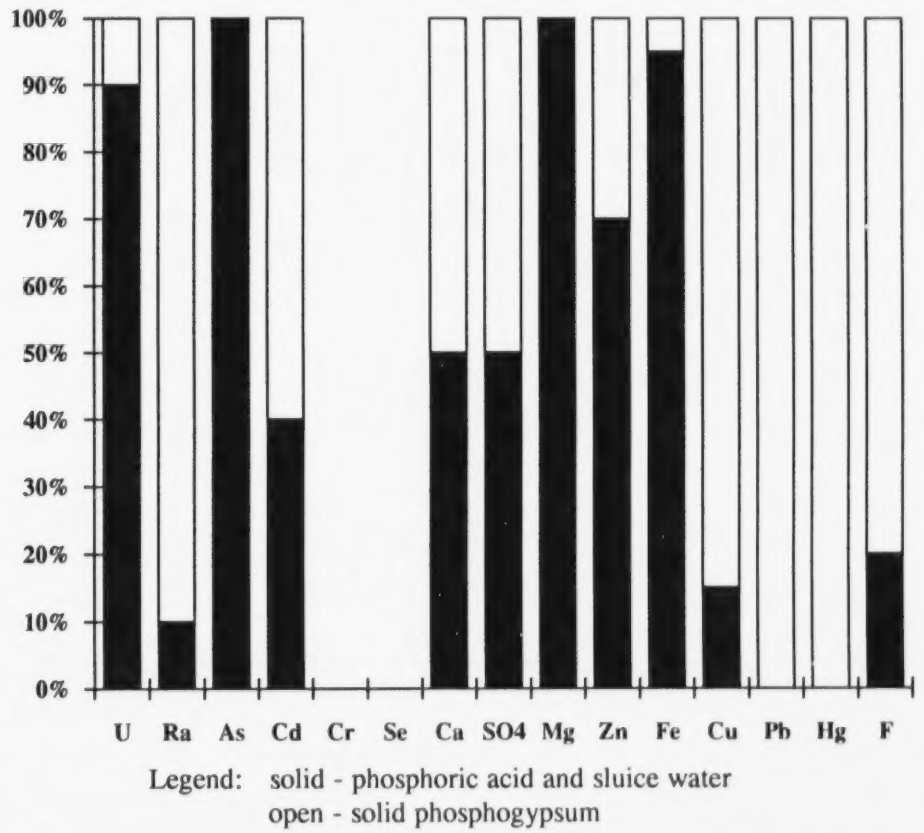
$$\text{osmotic pressure (bars @ } 25^{o}\text{C)} = 0.39 * \text{E.C.}$$

(Bower and Wilcox, 1965)

Using these equations we find that I = $2.99*10^{-1}$ mol L^{-1}, [salt] = $1.47*10^{4}$ mg L^{-1}, and osmotic pressure = 8.97 bars @ 25°C.

3. Chemical Constituents

As previously indicated the acidic nature of the sluice water brings with it high levels of soluble salts and trace elements. The acidic conditions along with different partitioning for each individual contaminant, between solid and liquid phase, contribute to the initial concentrations of elements determined in the sluice water. Figure 6 illustrates the partitioning of various components of the phosphate rock and how, due to processing, these components are partitioned into product acid and waste phosphogypsum.



Data collected from Becker 1989, Alloway 1990, O'Neill 1990, Lardinoye et. al. 1982, and Roessler et. al. 1979. Chromium and selenium have not been partitioned due to insufficient data.

Figure 6. Partitioning of contaminants between solid and liquid phase.

i. Major Elements

Sulfate levels found in the sluice water are high at 8600 mg L^{-1}. Table 3 shows that this concentration is approximately 17 x higher than maximum allowable concentrations (M.A.C.) in drinking water. There are concerns that sulfate could migrate off site and enter groundwater systems.

Initial levels of calcium indicate concentrations near 800 mg L^{-1}. Other major elements analyzed in the characterization study include magnesium, sodium, and potassium. Preliminary results show these levels at 11 mg L^{-1}, 1200 mg L^{-1}, and 30 mg L^{-1}, respectively.

Fluoride levels as seen in table 3 are very high relative to drinking water guidelines. At 4700 mg L^{-1} fluoride is approximately 3.5 orders of magnitude above guidelines and raises serious concerns. Partitioning of fluoride (Fig. 6) shows that approximately 20 % of the fluoride ends up in the product acid and thus in the waste sluice water.

ii. Radionuclides

As indicated, radionuclides are another constituent of concern. Rock phosphate contains uranium bearing minerals and during beneficiation the uranium is concentrated in the ground rock. During processing the uranium and its daughter product radium, (Fig. 6) are partitioned into the acid and solid phase. The radionuclides of major interest include U-238 measured from Th-234, and Ra-226 measured from Bi-214 and Pb-214 activities. As figure 6 shows, the Ra-226 is partitioned almost entirely into the solid phosphogypsum. Initial gamma-ray analysis of sluice water (Fig. 7) confirms the absence of Ra-226. This radionuclide therefore no longer plays a role in this study. The gamma spectrum illustrates that U-238 from Th-234, is found in the sluice water (Fig. 7) in elevated concentrations over the distilled water background sample (Fig. 8). Partitioning shows that U-238 is nearly 90 % directed into the product acid and therefore uranium is of concern in this study. The initial concentration of U found in the sluice water is approximately 3.5 mg L^{-1} using ICP and approximately 36 Bq L^{-1} U-238 using gamma spectroscopy (Fig. 7). At present time there are no guidelines set for U-238 maximum allowable levels in groundwater although regulations are currently being developed for this element.

The Canadian maximum allowable concentration of uranium in drinking water is 0.02 mg L^{-1} which is more than two orders of magnitude less than that found in the sluice water. Uranium is thus a key element in the studies conducted here.

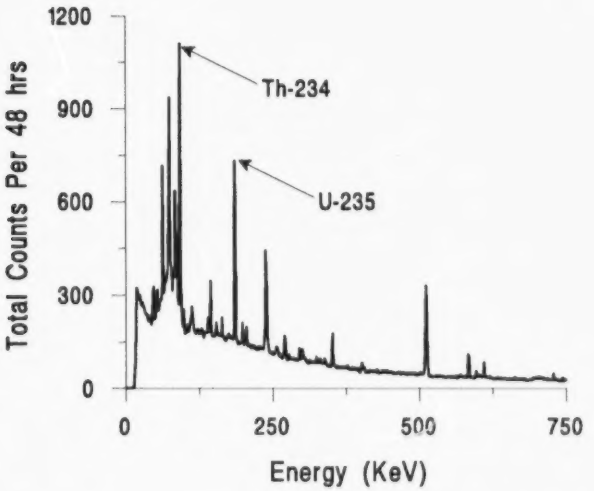


Figure 7: Gamma spectrum for phosphogypsum sluice water.

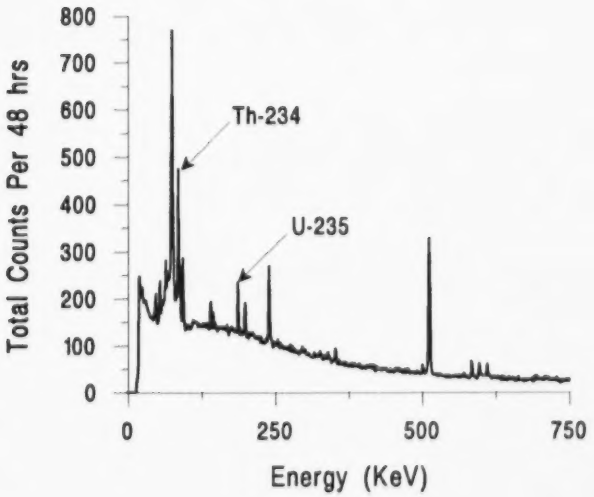


Figure 8: Gamma spectrum for distilled water background sample.

Figure 7 and 8 also shows high activity for U-235 at 186 KeV. U-235 at this energy level is not a true representation due to interference with Ra-226 at the same energy. Therefore this γ-ray energy is omitted. U-235 is also found to be only a very small fraction of total uranium so it is of little concern.

iii. Trace Elements

Concentration of some trace elements are found to be elevated in the sluice water (Table 3). The main elements considered in this study are As, Cd, Cr, and Se. As Figure 6 illustrates, the partitioning of arsenic is mainly into the acid, and thus the liquid sluice water phase. Cadmium is partitioned 40% into the acid or sluice water. Information on partitioning of selenium and chromium are not readily available.

Soluble arsenic levels found in the sluice water are at concentrations of 1.3 mg L^{-1} at the initial pH of 1.6. This level represents just under 2 orders of magnitude higher than allowed by both Canadian and U.S. drinking water guidelines. The concentration of 1.3 mg L^{-1} is however 3 times less than the environmental protection agency effluent maximum contaminant concentration (EPA E.M.C.C.) of 5.0 mg L^{-1}. Potential problems could arise if the soluble levels of arsenic reach groundwater and contaminate drinking water supplies.

Cadmium concentrations are also elevated over drinking water guidelines by approximately 3 orders of magnitude with respect to Canadian guidelines and 2 orders of magnitude with respect to U.S. guidelines. Cadmium measured at 2.0 mg L^{-1} is also 2 times higher than EPA E.M.C.C.. The high soluble levels of Cd with respect to drinking water guidelines illustrates the need for information on the sorption of this element as the sluice water passes through calcareous subsoils and/or lime or clay liners at waste repositories.

There is no apparent data available on the partitioning of chromium and selenium between solid and liquid phases but their relatively high initial soluble levels dictate their importance in the study. Chromium levels at 1.8 mg L^{-1} is almost 2 orders of magnitude higher than Canadian M.A.C.. Table 3 does however show that like arsenic, chromium is 3 times lower in sluice water than the EPA E.M.C.C.. Chromium, if found as a mobile species, does have the possibility of causing a negative environmental impact.

The soluble selenium levels in the phosphogypsum sluice water are also of concern. Initial concentrations of 0.7 mg L^{-1} are 70 times higher than both Canadian and U.S. drinking water guidelines. Levels are very close to the EPA E.M.C.C..

B. Elemental Chemistry, Solubility Equilibria, and Computer Speciation

Each element of concern is examined in both chemical neutralization and soil adsorption experiments and the results of each are presented in graphical form. Elemental data will be illustrated as solution concentration versus pH. Results show average values and give statistical variation ranges. Total soluble levels of each element will be examined over the pH range with emphasis on trends exhibited. Areas of maximum and minimum solubility will be identified. Speciation of the elements will be presented based on the GEOCHEM computations, and solubility controlling solids of the key elements will be illustrated in specific diagrams.

Due to the acidic nature of the phosphogypsum sluice water, we see high soluble levels of all contaminants. Thus, the worst case scenario of maximum negative environmental impact is associated with the initial sluice water. In nature, as the sluice water leaches through the subsoil the pH is buffered and approaches neutrality. In environments such as Alberta's much of the subsurface contains calcareous layers and the final pH reached by the infiltrating sluice water would be around pH 8. This would also be true for phosphogypsum waste repositories utilizing calcareous and clay liners. As the pH increases from acidic through neutrality and into the alkaline range there are associated responses by each individual contaminant. Precipitation and formation of insoluble minerals and/or co-precipitation of contaminants with other minerals play an important role in decreasing soluble contaminant levels and therefore decreasing mobility through the subsurface or liners and preventing groundwater contamination. Three areas which are examined and whose results will be discussed include: overall chemical neutralization effects on specific contaminant levels; observed solubility controlling solids which may or may not control the level of contaminants, and predicted speciation of each element of concern over the pH range of the experiment to identify mobile and sorbed species.

Soil adsorption experiments are utilized in order to understand how the sluice water reacts with soil minerals. We must keep in mind that data presented with respect to the adsorption experiment do not mean that only adsorption of the element onto soil material has occurred. The acidic sluice water may have reacted causing dissolution of clay minerals releasing mineral constituent ions which then could have reacted with trace elements of concern resulting in attenuation by precipitation. Reaction of sluice water with soil clays also causes pH buffering resulting in neutralization and concomitant precipitation rather than strictly attenuation by adsorption.

1. Major Elements

i. Calcium

Calcium is the major cation present in phosphogypsum sluice water but is of little environmental concern. Where this ion does come into play is when it becomes complexed with environmentally sensitive anions such as SO_4^{-2}, PO_4^{-3}, SeO_3^{-2}, and arsenates.

Calcium is present at a concentration of approximately 850 mg L^{-1} in the initial sluice water. Figure 9 shows that calcium concentration fluctuates over the pH range of the experiment with highest levels being 1400 mg L^{-1} at pH 2.4. By examining both figure 9 and 12 together we can see that calcium levels, as expected, are partly responsible for sulfate levels. At pH 2 - 3 we see the highest calcium and lowest sulfate. Also a decrease in soluble calcium concentration at pH 3 - 6.5 corresponds to an increase in soluble sulfate levels. In the alkaline range an increase in calcium again causes a decrease in sulfate levels.

Figure 10 presents a solubility controlling diagram for the prediction of soluble calcium concentrations at differing sulfate levels. The data points for Ca^{+2} and SO_4^{-2} activities of this study follows the gypsum solubility isoline represented in the diagram. This shows that in this study the sluice water's calcium and sulfate concentrations, throughout the treatments, are controlled by gypsum.

Calcium and sulfate are studied together due to their expected dependency on gypsum solubility. Figure 11 includes a gypsum solubility equilibrium isoline. Our results show that the sluice water is at or near saturation relative to gypsum

giving evidence that gypsum controls the activities of Ca^{+2} and SO_4^{-2}. Gypsum is the dominant mineral making up the waste phosphogypsum and thus experimental data of this study are consistent with theoretical considerations.

At all pH values Ca^{+2} activity is controlled by gypsum (Fig. 12). We can follow each data point and reference it to SO_4^{-2} activities to determine if the treatment is at saturation or over/under saturated with respect to the controlling solid gypsum. It does not appear that both $CaSO_4 \cdot 2H_2O$ (s) and $CaCO_3$ (s) were existing in the system together. If that were the case, Ca^{+2} concentration would follow the $CaCO_3$ (s) solubility isoline (Fig. 11) after pH 8.

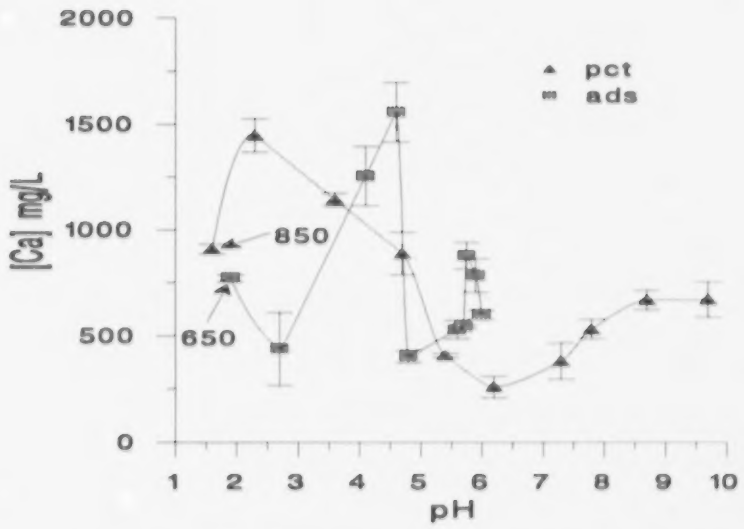
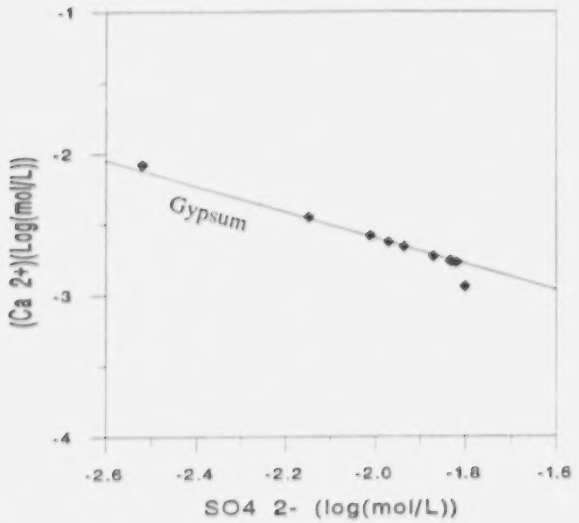


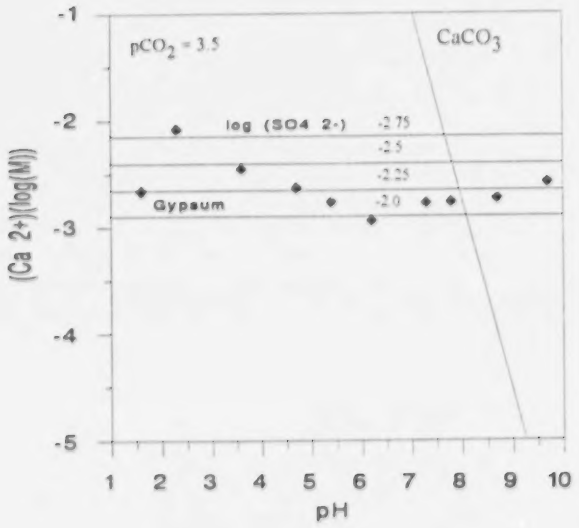
Figure 9. Soluble calcium concentration (mg L^{-1}) versus change in pH.

Figure 11 also shows calcium activity versus pH and again indicates that gypsum is the controlling mineral. $CaCO_3$ (s) has been proposed as a controlling solid at pH > 7.5 but our results indicate that gypsum at differing sulfate activities may be the only calcium control at least during the early stages of neutralization of sluice water.



Thermodynamic data from Lindsay (1979).

Figure 10. Gypsum solubility equilibrium with neutralization experiment.



Thermodynamic data from Lindsay (1979).

Figure 11. Solubility equilibria of some calcium minerals with neutralization data.

ii. Sulfate

Results show that sulfate is exceptionally elevated at 8600 mg L^{-1}. With neutralization from pH 1.6 to 9.9 there is a trend of decreasing concentration with subsequent increase and leveling off between pH 6-9 (Fig. 12). A rapid decrease in concentration from pH 1.6 to 2.4 is evident. At pH 2.4 the sulfate concentration is approximately 2500 mg L^{-1}. This also represents the pH of minimum solubility of sulfate minerals. Above pH 2.4 soluble levels increase up to 4300 mg L^{-1} at pH 5 then levels off at this concentration throughout the neutral and alkaline range up to pH 9. At pH greater than 9 a decrease in solubility is again evident as concentration drops off. Therefore we see minimum sulfate solubility at pH 2 and at pH $>$ 9 and maximum solubility at pH $<$ 2 and between pH 4 and 9.

The mobility of sulfate may be quite high at neutral pH and calcareous subsoils may not lower SO_4^{-2} concentrations below 4000 mg L^{-1}. The major anion SO_4^{-2} may not be significantly attenuated by precipitation reactions. Lewis (1986) found that removal of sulfate from phosphogypsum leachate was less affected by pH. Results show similar trends with those identified in Murray and Lewis (1985) showing lowest SO_4^{-2} concentration around pH 2 - 3.5. Reduced precipitation above pH 3.5 may be due to formation of mobile $CaSO_4^o$. Precipitation increases at pH in the alkaline range due to increases in calcium ion and formation of $CaSO_4 \cdot 2H_2O$ (s). In calcareous systems at high pH, precipitation as gypsum appears to be the major removal mechanism for sulfate (Fig. 11). Adsorption of sulfate with soil shows similar results (Fig. 12) with the most significant adsorption seen between pH 2.5 and 4.5 (Fig. 13).

To more clearly illustrate adsorption, graphs were constructed for all elements using data found in the elemental concentration versus change in pH graphs. The graphs were created by simply plotting the difference between the precipitation and adsorption concentration at each selected pH value. Adsorption plays a slight role in sulfate attenuation around pH 2.5 - 4.5 (Fig. 13) where approximately 1000 mg L^{-1} is adsorbed. The main removal mechanism, however, appears to be formation of gypsum. Due to the relatively high levels of soluble sulfate this is one element which may cause significant negative environmental impact. Natural attenuation in the subsurface environment may not be sufficient to reduce sulfate levels below regulatory limits. Waste management

practices may be required to reduce levels further to prevent groundwater contamination.

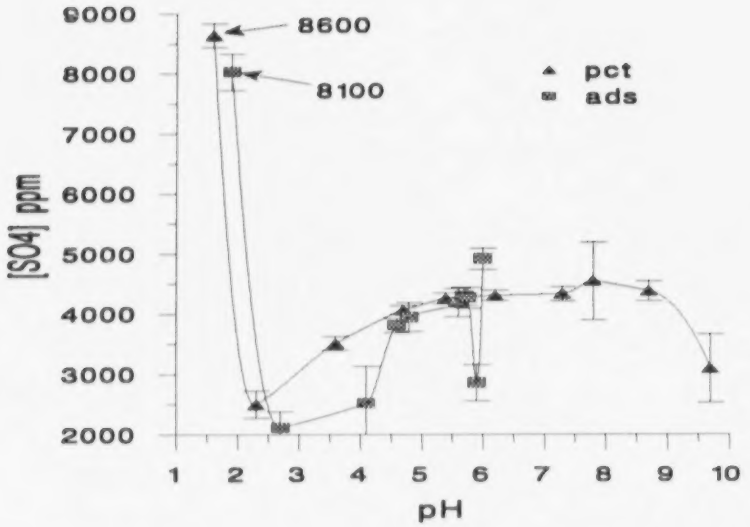


Figure 12. Soluble sulfate concentration (mg L^{-1}) versus change in pH.

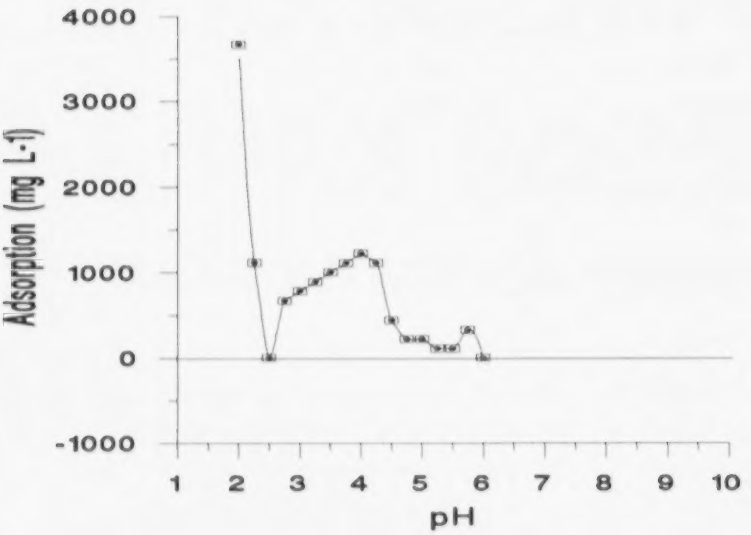


Figure 13. Adsorption curve for sulfate in relation to solution pH.

iii. Phosphate

Phosphate is another anion in relatively high concentration in the sluice water. Phosphate (PO_4^{-3}) is present as residual product acid which has escaped filtration and moved along with the phosphogypsum waste. The effects of chemical neutralization on phosphate levels is seen in figure 14. Phosphate levels are high in the acid range from pH 1.6 - 4. Maximum concentration of 480 mg P L^{-1} is seen at pH 2.4 with a nearly linear decrease to detection limits at pH 6.5. There is virtually no phosphate present in solution at pH > 6.5.

Figure 14 shows that adsorption (reaction with clay) plays a minor role in phosphorous removal especially in the pH range greater than 3. Lewis (1986) illustrated that pH of the system appears to be the controlling factor in the removal of orthophosphate from phosphogypsum leachate solutions. The pH plays a role in the speciation of the phosphate thereby determining possible complex forming ions. System pH also plays a role in adsorption by, again, determining the species present and the charge on the species as well as the surface charge on the adsorption medium. In this study precipitation rather than adsorption is the major control. It is also possible that for strongly acidic conditions, some weathering of clays occur releasing aluminum which then combines with phosphate to form insoluble Al-phosphates.

iv. Iron

The initial sluice water at pH 1.6 shows levels of Fe (III) at 125 mg L^{-1} (Fig. 15). The concentration drops off rapidly to detection limits as pH increases to pH 3.5. Soluble iron levels are also of concern in the phosphogypsum sluice water, not for an environmental reason directly, but as an available cation for further complexing with anions of relevance. Iron minerals play an important role in adsorption of trace elements and will be discussed in subsequent sections.

Again as with calcium and phosphorous, adsorption follows a nearly identical trend to chemical neutralization. Reaction of sluice water with clay at pH 2.5-3 increases Fe concentration, possibly due to some dissolution of iron containing clay minerals or even primary minerals.

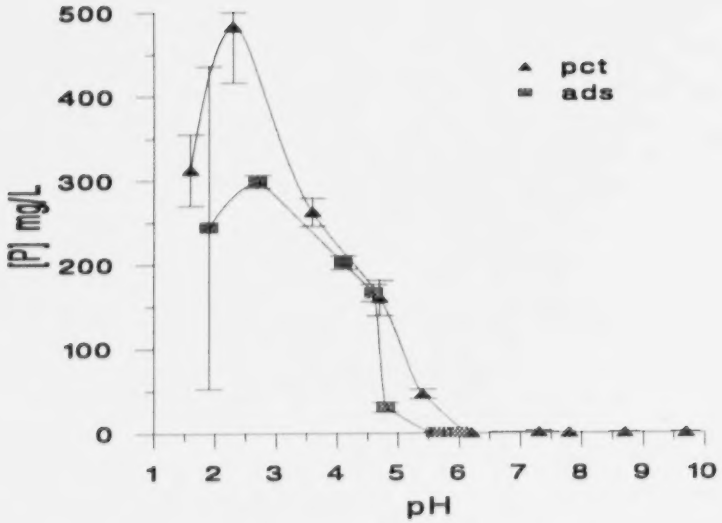


Figure 14. Soluble phosphorous concentration (mg L^{-1}) versus change in pH.

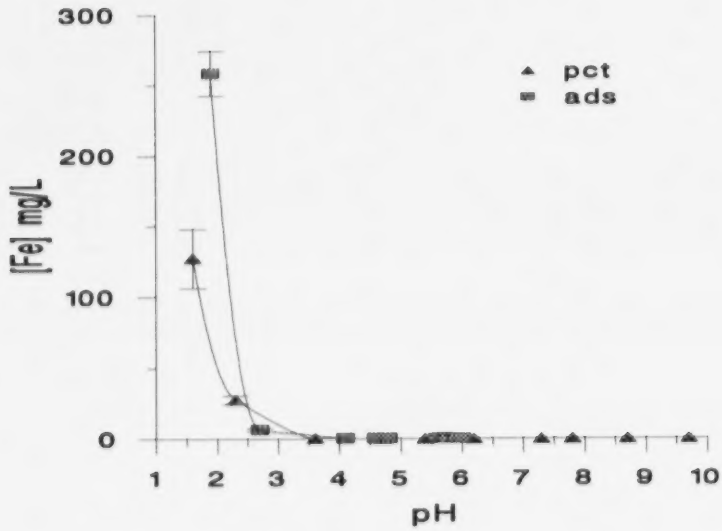
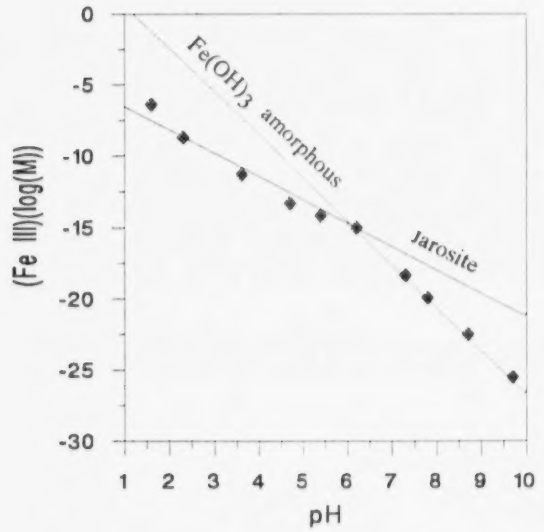


Figure 15. Soluble iron concentration (mg L^{-1}) versus change in pH.

Iron is assumed to be in the Fe(III) oxidation state, consistent with the phosphogypsum waste leaching environment. Ferric ion activity is therefore used for the solubility controlling diagram (Fig. 16). The diagram shows that at pH < 6 jarosite is the controlling solid and amorphous $Fe(OH)_3$ controls activity at pH > 6.

As evident in Figure 16 aqueous concentrations of iron are controlled primarily by precipitation/dissolution reactions rather than adsorption/desorption (Rai, et.al., 1987). Dissolved Fe(III) concentrations are controlled by the solubility product of jarosite and amorphous $Fe(OH)_3$ (Fig. 16). Jarosite ($KFe_2(SO_4)(OH)_6$(s)) is a sulfate mineral and has been identified as a weathering product in acid mine drainage environments (Nordstrom, 1982). Rai, et. al. (1987) has also found jarosite to be common for acidic systems involving pyrite oxidation products in coal cleaning wastes. We can therefore conclude that both amorphous $Fe(OH)_3$ and jarosite can be predicted as solubility controlling solids for Fe in this study.



Thermodynamic data from Lindsay (1979).

Figure 16. Solubility equilibria of some iron minerals with neutralization data.

v. Fluoride precipitation

Initial fluoride investigations show levels of fluoride at 4700 mg L-1 for the raw sluice water at pH 1.6 (Fig. 17). This high concentration decreases at pH > 3 and establishes a constant concentration around 18 mg L-1 throughout the remaining pH range of the experiment.

The study shows that under extremely acidic conditions such as those of phosphogypsum sluice water, fluoride is at toxic levels and migration off site into surface and/or groundwater could be hazardous. Leaching of the sluice water through calcareous subsoils as found at waste repositories within Alberta would however result in an increase in sluice pH to approximately pH 7-8.5 and at this range the concentration of fluoride should be around 13 mg L^{-1} based on results of this study (Fig. 17), which is still 10x higher than allowable for drinking water.

The major mechanism responsible for the decrease in aqueous fluoride concentration is precipitation as CaF_2 (s) (fluorite). This is expected due to the high concentration of both F^- and Ca^{+2} resulting in near complete F removal. Murray and Lewis (1985) found almost complete fluoride removal in a carbonate system at pH 4.5. They also determined that the critical precipitation pH is 3.8.

Figure 18 illustrates some possible fluoride solubility controlling solids. The most likely solubility control for the sluice water system is fluorite (CaF_2)(s). Fluorite maintains free ion fluoride activity at approximately -3.5 to -4.5 log M depending on calcium ion concentration. As figure 18 shows, the level of free ion fluoride is approximately -3.25 log M and indicates that fluorite is the likely controlling solid. Other solubility controls, fluorapatite and iron and aluminum fluoride solids do not appear to be relevant in this study under the conditions of the experiment.

Results of previous studies have shown similar findings in that fluorite is the solid phase that controls F activity especially within calcareous soil environments. It is the activity of calcium ion which regulate fluorite precipitation and some studies (Muthukumar and Subrahmanyam, 1987) have examined the possibility of additions of excess lime for the safe removal of F to around 8 mg L^{-1}. Use of gypsum alone results in 20 mg L^{-1}.

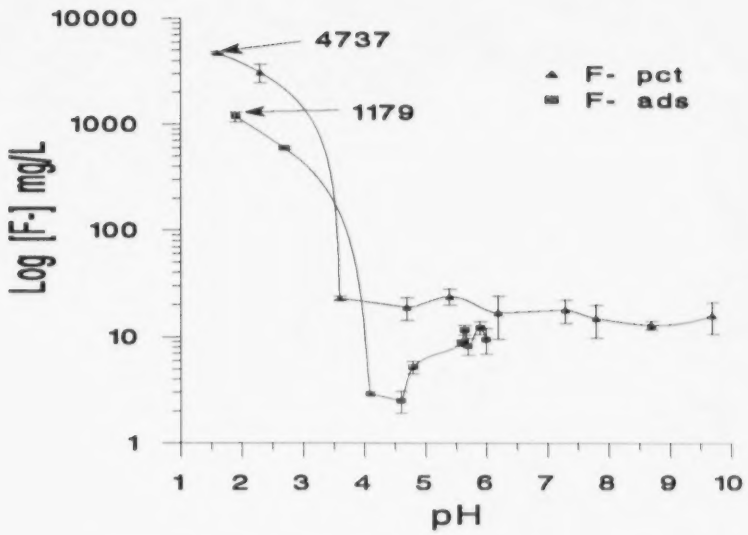


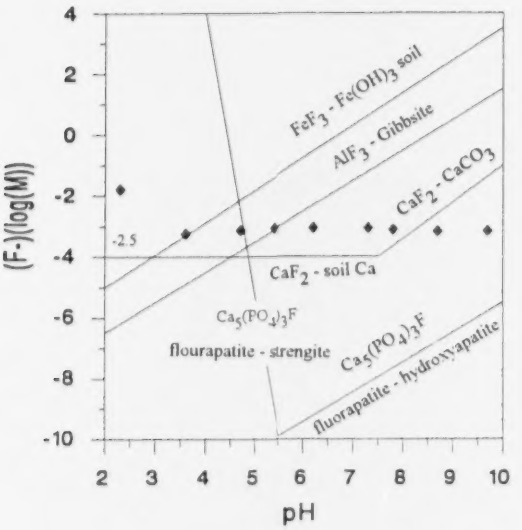
Figure 17. Soluble fluoride concentration (mg L^{-1}) versus change in pH.

Aluminum was not measured in this study so AlF_3 (s) cannot be ruled out as a possible fluoride control although our data (Fig. 18) shows fluoride ion activities to represent a nearly parallel trend to the fluorite solubility isolines. The slightly higher F^- activity measured in this study versus activity based on the solubility product of fluorite could be due to the degree of crystallinity and purity of the CaF_2 precipitate formed during the equilibration. Alternatively, the solution may be slightly supersaturated with respect to fluorite (Fig. 18).

There is the hazard of fluorite resolublization if there is not adequate amounts of calcium present to maintain solid phase stability. This would be prevalent if there were continued leaching of fluoride rich sluice water in a carbonate exhausted environment. This would then pose off site fluoride migration concerns.

The speciation of fluoride changes drastically from pH 1.6 to 4 where initially in the strong acid range, the neutral ion pair HF^o dominates at approximately 75% of total fluoride in solution. Free ion F^- makes up approximately 5% at pH 1.6 (Fig. 19). As pH increases there is a sharp decline in HF^o neutral ion pair to 0% at pH 4.6 whereas F^- increases at the same rate and is the only complex found in solution at pH > 4.6. Negatively charged calcium

fluoride ion pairs play a very minor role in fluoride speciation throughout the entire pH range.



Thermodynamic data from Elrashidi and Lindsay (1986).

Figure 18. Solubility equilibria of some fluoride minerals with neutralization data.

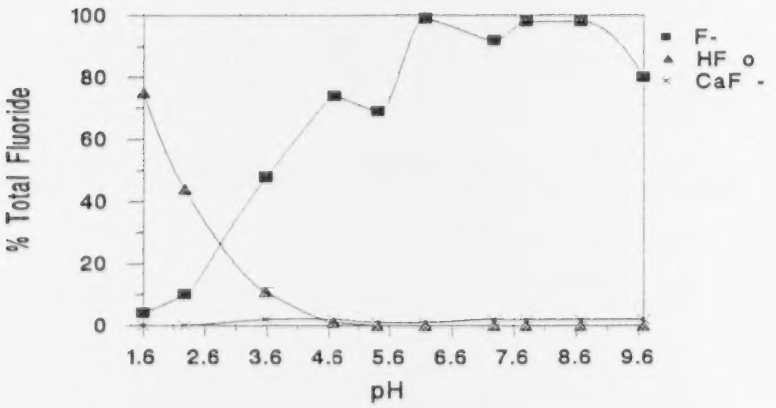


Figure 19. GEOCHEM predicted speciation of fluoride following neutralization.

The speciation reported in figures 19 and 21 are the result of the information inputted into the GEOCHEM modeling program. These are predicted species and they may change depending on the elements involved. Aluminum was not an element measured in the study and therefore aluminum fluoride complexes are not predicted although they may in fact be present. However, aqueous concentrations of Al are not likely to exceed a few ppm in the neutral pH ranges where F^- concentrations are about 13 mg L^{-1}. Even if a few ppm Al are present a large amount of the soluble F^- would occur as the ion pairs depicted in Figure 19.

Our study does however show the importance of free ion F^- and neutral HF^o as dominant forms. In the pH range of high fluoride concentration (< pH 3.5) we see decreasing dominance of HF^o and increasing dominance of F^- with increasing pH from an initial pH of 1.6 to pH 3.5 (Fig. 19). At pH > 4, F^- is the predominant species agreeing with work done by Elrashidi and Lindsay (1986).

vi. Fluoride adsorption

The results of adsorption (or reaction with mineral material) on fluoride soluble concentration can be seen in both figures 17 and 20. We see that the lowest concentration due to maximum adsorption or reaction with minerals is at the lowest pH and as pH increases adsorption decreases. At pH < 3 adsorption values reach up to 2000 mg L^{-1} and at pH > 4 adsorption levels off at 10 - 15 mg L^{-1}. While adsorption is involved in this discussion of data, one can not preclude chemical precipitation of F^- caused by reaction of soil minerals and release of elements which react with F^- to bring a reduction in soluble levels.

Bar-Yosef, et.al. (1989) found in their study similar results to those found in this adsorption experiment. Adsorption was greatest at the lowest pH and decreased with increasing pH. They found adsorption to be negligible at higher pH values. Adsorption is also greater with increasing clay content. Amorphous Al is a very important component of F sorption (Peek and Volk, 1985). Fluoride adsorption with clay minerals involves ligand exchange with OH groups. It is also proven that kaolinite and gibbsite are better adsorbers than montmorillonite and vermiculite which has bearing on the type of clay liners suitable for waste repositories. The most suitable soils for F adsorption are those with low to

intermediate pH, low E.C., and high content of low CEC clays (Bar-Yosef, et.al., 1989).

By pH 4, adsorption of F is minimal compared to the adsorption at lower pH values (Fig. 20). This may be due to an increased precipitation effect starting at this pH. Murray and Lewis (1985) found this pH to be the critical precipitation value.

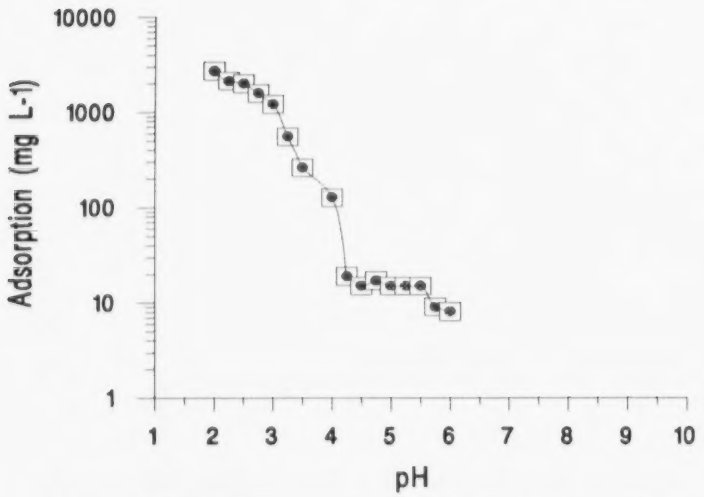


Figure 20. Adsorption curve for fluoride in relation to solution pH.

The speciation of fluoride following the adsorption experiment (Fig. 21) shows similar results to those found following neutralization (Fig. 19). Under acid conditions neutral HF is slightly more dominant at 30% than the other complexes, FeF^{+2} at 15% and F^- at 5%. Again as pH increases F^- becomes the only relevant species.

From other studies (Elrashidi and Lindsay, 1986) aluminum fluoride complexes are known to play an important role in speciation but as previously discussed, aluminum was not included in this study. Positively charged iron fluoride does play a minor role (Fig. 21) probably due to increased iron concentration attained from soil exchange and weathering reactions. As with previous speciation calculations, free ion F^- plays the dominant role and would be the soluble form in solution and available for migration or plant uptake.

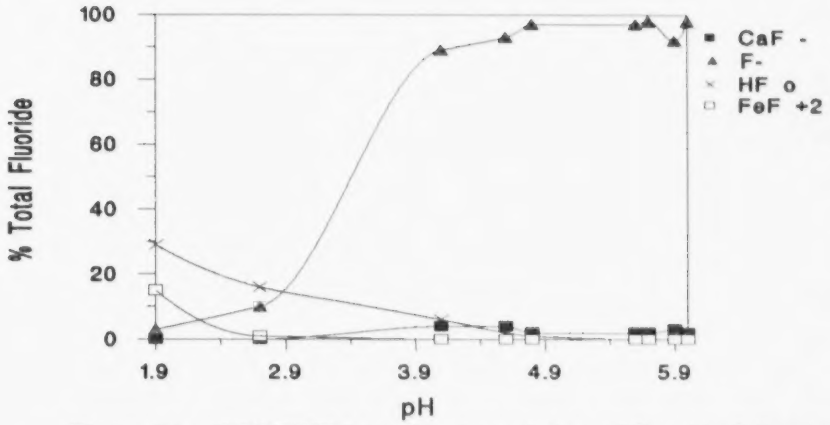


Figure 21. GEOCHEM predicted speciation of fluoride following adsorption.

2. Radionuclides

Uranium

One of the main focuses of this study deals with radionuclides present in the sluice water. Very few studies have examined the levels and attenuation of radionuclides at phosphogypsum waste disposal sites and increasing interest for groundwater safety has prompted concern. The system pH is the prime variable controlling uranium concentrations and speciation (White, et. al., 1984 and Morin, et.al., 1988). Studies have shown uranium to be moderately mobile in oxidizing conditions across the whole pH range. In shallow groundwater oxidizing conditions are expected and uranium behaves as U (VI) or UO_2^{+2} (Barney and Geiger, 1989). Under natural conditions an increased stability of U (VI) over U (IV) greatly increases mobility of uranium. U (IV) as U^{+4} tends to precipitate as insoluble uranites and/or coffinite (Langmuir, 1978). Langmuir (1978) also points out that in natural waters uranium is complexed with CO_3, OH, PO_4, F, SO_4, and SiO_4, and these increase the solubility of uranium minerals and increase mobility. The majority of studies done have been in natural systems rather than under laboratory conditions and this gives rise to differing explanations for contaminant reduction. White, et. al. (1984) determined that groundwater dilution plays a large role in decreasing radionuclides to near-background levels.

Figures 22 and 23 show U-238 activities, determined from Th- 234 peaks, as both Bq L^{-1} and mg L^{-1}, respectively. Initial activities of 36.6 Bq L^{-1} or 2.54 mg L^{-1} as determined by gamma spectroscopy and an initial concentration of uranium of 3.48 mg L^{-1} (Fig. 23) determined by I.C.P. represent an increase by 2 orders of magnitude over allowable drinking water guidelines. All three measures of uranium solution concentration versus pH show the same trend in that concentration drops off sharply to detection limits at pH 3.5 (Fig. 22,23,24). Beyond pH 3.5 with further chemical neutralization there is no detectable uranium found in solution.

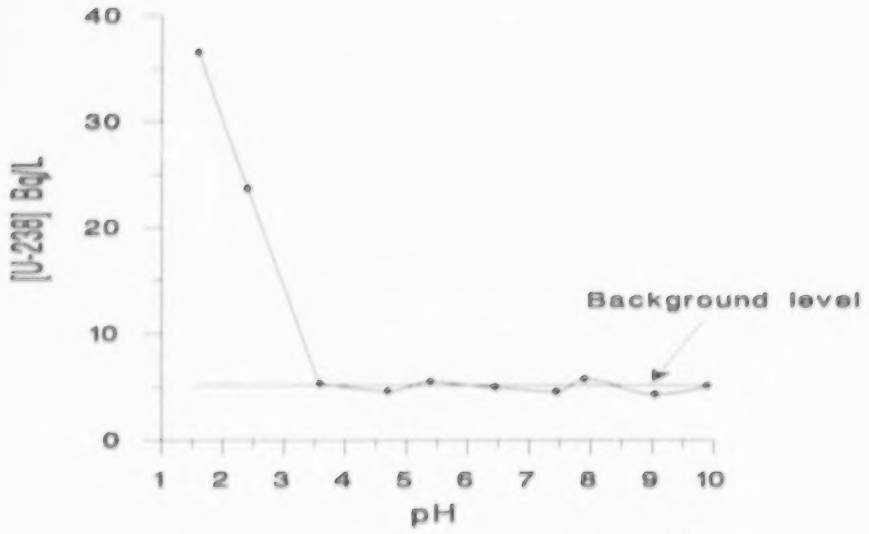


Figure 22. Soluble U-238 activity (Bq L^{-1}) versus change in pH.

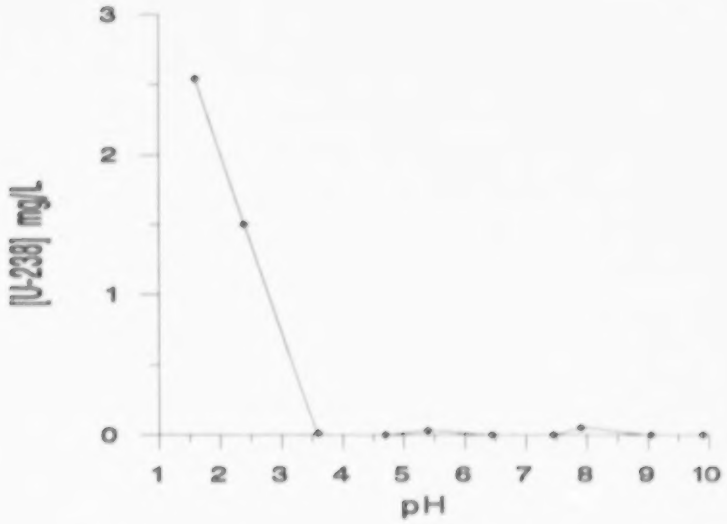


Figure 23. Soluble U-238 concentration (mg L^{-1}) versus change in pH.

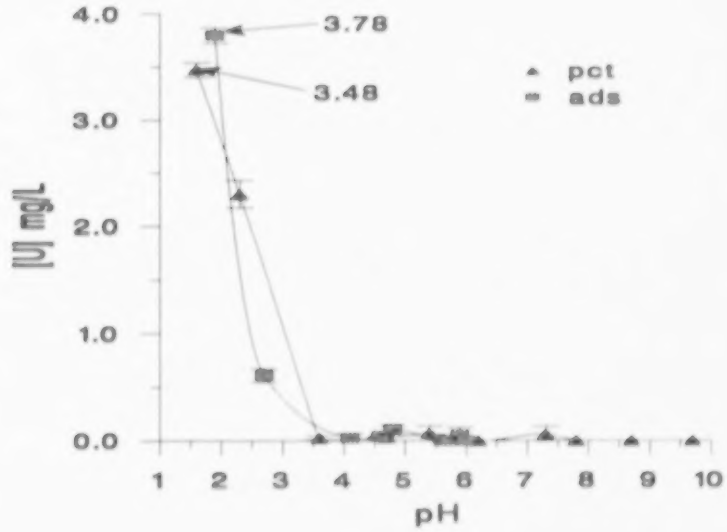


Figure 24. Soluble uranium concentration (mg L^{-1}) versus change in pH.

These results show that, as with other studies, pH is the main factor in attenuation of uranium. Uranium concentration dropped rapidly to near detection

limits at pH 3.5 (Fig. 24). In the pH range of 1.9 - 3.5 uranium speciates as uranous fluoride complexes. $UO_2F_3^-$ dominates up to pH 3 and then $UO_2F_2^o$ at pH 3-7.5 (Fig. 25). The negatively charged and neutral species of uranium have the possibility to be mobile under acidic conditions.

Results of speciation calculations may identify uranium complexes which may occur in solution. At pH values greater than 3.5 there is very little uranium in solution so it is those species that appear prior to pH 3.5 which are important. Figure 25 and 26 illustrate that Uranium fluoride complexes make up the dominant species. $UO_2F_3^-$ is the major species in the acid range and at pH > 3 is replaced by $UO_2F_2^o$ as the dominant complex. UO_2F^+ plays a minor role in speciation comprising up to 20% of total uranium around pH 3.5. Under alkaline conditions uranium carbonate and uranium hydroxide complexes are most important (Fig. 26) but again under these pH conditions there is negligible amounts of uranium present in solution.

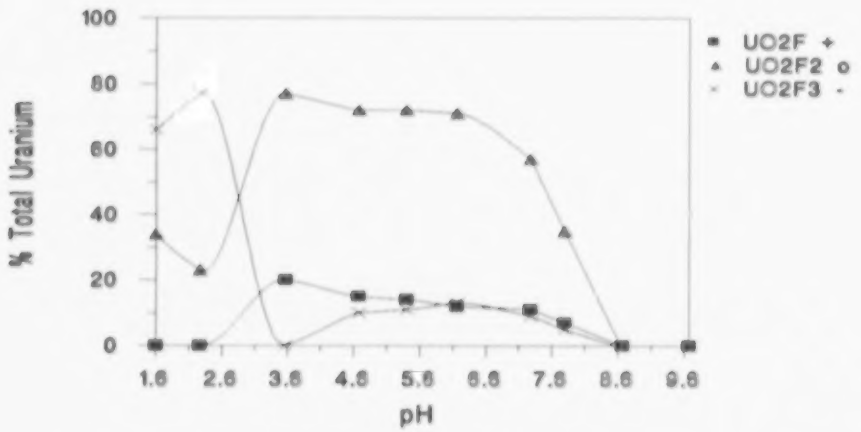


Figure 25. GEOCHEM predicted speciation of uranium following neutralization.

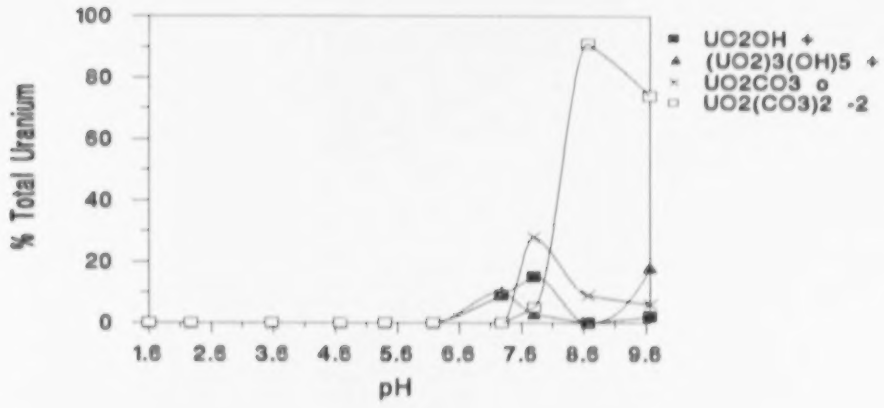


Figure 26. GEOCHEM predicted speciation of uranium following neutralization.

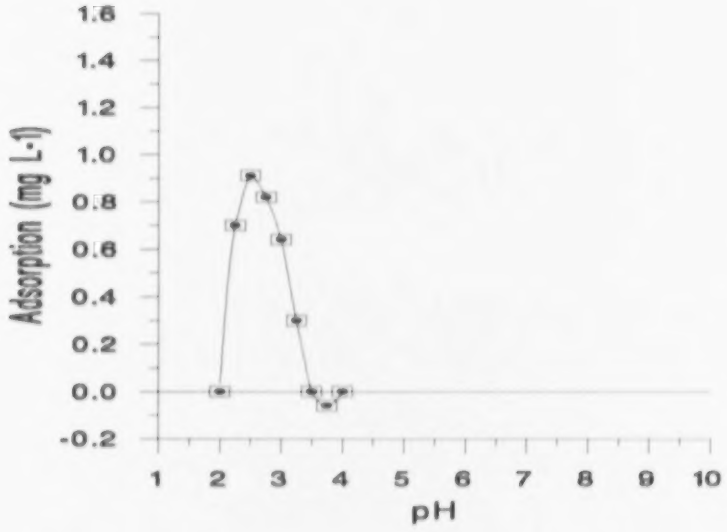


Figure 27. Adsorption curve for uranium in relation to solution pH.

Uranium adsorption appears much less significant in uranium control than the processes of precipitation. Figure 24 shows the uranium adsorption curve which has some similarities to the precipitation curve. However, there is some

adsorption (or attenuating reaction) in the pH range > 2 and < 3.5 up to a maximum of 0.9 mg L^{-1} U at pH ~ 2.5 (Fig. 27).

Uranium speciation for the adsorption experiment is similar to results for the precipitation experiment. Again there is domination of both $UO_2F_3^-$ and $UO_2F_2^o$ with increasing UO_2F^+ ion pairing from pH 2.9-3.5 (Fig. 28). Neutral UO_2F_2 comprises 40-60% of total uranium over the pH range of the adsorption experiment (Fig. 28). Negatively charged UO_2F_3 makes up 40% of total uranium under acid conditions (pH 2-3) then decreases in importance as pH increases. At pH > 3 UO_2F^+ becomes increasingly important and accommodates 20-40% of total uranium.

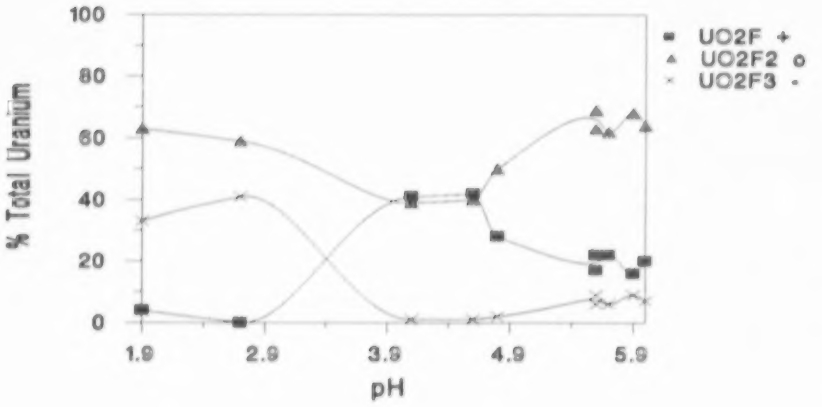


Figure 28. GEOCHEM predicted speciation of uranium following adsorption.

3. Trace Elements

i. Arsenic Precipitation

Results of the precipitation experiment show how soluble levels of arsenic decrease in response to chemical neutralization. The initial acidic sluice water contained 1.29 mg As L^{-1} (Fig. 29). Over the pH range 1.6 to 5 the

concentration fluctuates from 1.3 to 1.0 mg L-1. At pH 5 the concentration of As is 1.2 mg L-1 and with further increase in pH to 8 a nearly linear decrease occurs in concentration to 0.15 mg L^{-1}. Further increase in pH has little effect on As concentration.

Several studies have been carried out examining the behavior of arsenic in response to chemical neutralization. Arsenic is one element which undergoes redox changes. Arsenic can be found in the +3 and +5 oxidation states. Under oxidizing conditions, which are expected in a waste leaching environment, arsenic is found as +5 arsenates (AsO_4^{-3})(Alloway, 1990). That is the form expected in phosphogypsum sluice water and is therefore the form which will be included in speciation calculations.

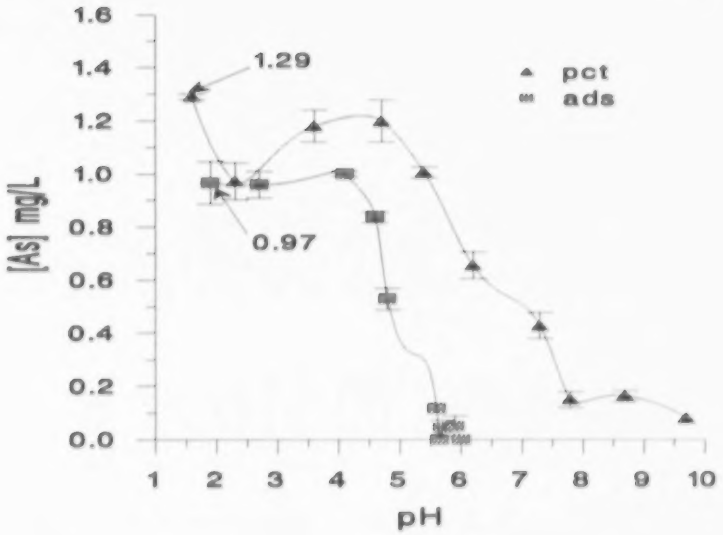
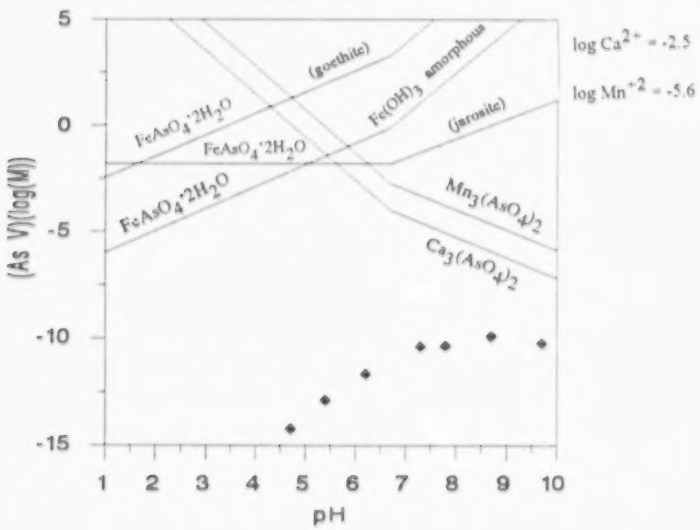


Figure 29. Soluble arsenic concentration (mg L^{-1}) versus change in pH.

Arsenic shows measurable levels throughout the pH range of this study. As Figure 30 illustrates, the activities of As (V) are much lower than the Ksp's of the candidate arsenic minerals. These minerals do not control the aqueous concentration of arsenic in the experiment. Arsenic (V) shows activities of -15 to -10 log M over a pH range of 2-7.

Precipitation of these minerals (Fig. 30) is therefore not expected due to the solution being greatly undersaturated with respect to the minerals. Precipitation may occur if there is a undetermined solubility controlling solid which follows the same trend as arsenic activities. This is not expected. What is most likely occurring is co-precipitation of arsenic with other minerals and/or sorption of arsenates on precipitated Fe and Al minerals (Livesey and Huang, 1980). Sorption may be the most important arsenic controlling mechanism and will be discussed later with respect to the adsorption experiment. Other studies have shown that in acidic environments $Mn_3(AsO_4)_2$ (s) is the most stable mineral and under alkaline conditions $Ca_3(AsO_4)_2$ (s) is most stable. Other minerals in decreasing stability are Cd > Pb > Cu > Al > Fe > Zn > Ni arsenates (Sadiq, et. al., 1983; Hess and Blanchar, 1976). Our results show that these minerals will however not form at the ion concentrations found in the sluice water.



Thermodynamic data from Hess and Blanchar (1976), Sadiq, et.al. (1983), and Lindsay (1979)

Figure 30. Solubility equilibria of some arsenate minerals with neutralization data.

Arsenic in this experiment is seen to behave as anionic arsenate (As(V)). The species of arsenic is dependent on redox and pH. The species are important in determining bioavailability, sorption and/or migration potential. Figure 31 and 32 illustrates that speciation of As as arsenate changes over the pH range 1.6 to 9.9. Arsenic is present as $H_3AsO_4^o$ at pH 1.6 then changes to $H_2AsO_4^-$ at pH 2.4 to 6.6. At pH 6.6 $HAsO_4^{-2}$ replaces $H_2AsO_4^-$ as dominant species. Through this pH range As is present as $CaAsO_4^-$ at approximately 10% of the total As. At pH > 7.5 there is a change in speciation as $CaAsO_4^-$ replaces $HAsO_4^{-2}$ as the dominant species.

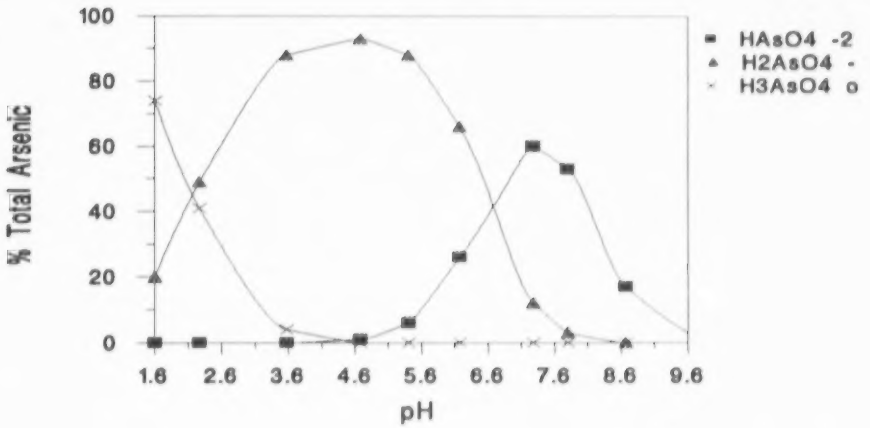


Figure 31. GEOCHEM predicted speciation of arsenic following neutralization.

The speciation of arsenic as predicted by GEOCHEM shows the dominant forms are $H_2AsO_4^-$ and $HAsO_4^{-2}$ under acidic and near neutral conditions, respectively (Fig. 31). The neutral species ($H_3AsO_4^o$) occurs under highly acidic conditions. This contrasts with the work done by Hess and Blanchar (1976) which showed that under acidic conditions $H_2AsO_4^-$ comprised 85 - 90% of total arsenic. Sadiq, et. al. (1983) also showed $H_2AsO_4^-$ made up ≅ 80% of total arsenic from pH 3 - 6. The increase in calcium arsenate ion pairing at alkaline pH could be due to high calcium levels in solution. There is very little arsenic found in solution at pH > 7 and it is for these alkaline pH values that $CaAsO_4^-$ could be the dominant species. The amount of this species is therefore considered

negligible. The most prevalent and mobile arsenic is found as $H_2AsO_4^-$. This may pose environmental problems in acidic environments but as results show, at alkaline pH, which is expected for Alberta subsoils, there would be little if any negative environmental impact.

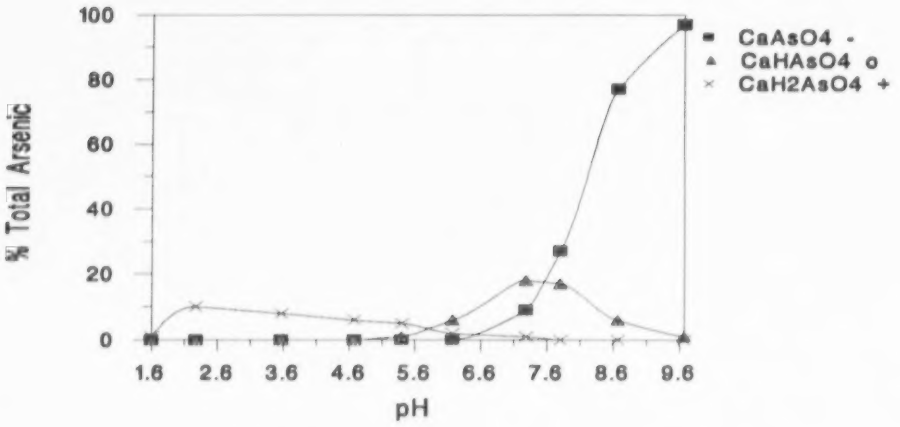


Figure 32. GEOCHEM predicted speciation of arsenic following neutralization.

ii. Arsenic Adsorption

Figure 29 shows that maximum adsorption of As occurs at pH 5 - 6. Very little if any adsorption is seen at pH < 3. Approximately 0.2 mg L^{-1} is removed due to adsorption at pH 3-4. At pH 4.5, 5, 5.5, and 6, the amounts of arsenic removed by adsorption mechanisms are 0.3, 0.75, 0.7, and 0.7 mg L^{-1} respectively (Fig. 33).

Adsorption / desorption appears to be the mechanism most responsible for attenuation of arsenic from phosphogypsum sluice water. Arsenic does not readily form positively charged ion pairs. Rather, arsenic is found as neutral or negatively charged ion pairs. Leaching of As is inhibited by hydrated Fe and Al oxides, clays, and organic matter (O'Neill, 1990). Jacobs, et. al. (1970) found arsenic adsorption was due to amorphous Al and Fe components.

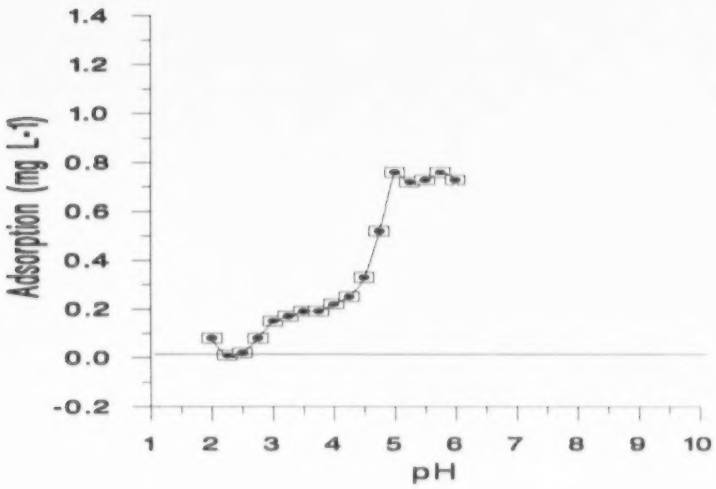


Figure 33. Adsorption curve for arsenic in relation to solution pH.

Speciation results predicted by GEOCHEM following adsorption are illustrated in figure 34 and 35. Hydrogen arsenates are the dominant species either as neutral $H_3AsO_4^o$ under highly acidic (pH < 2) conditions or $H_2AsO_4^-$ for pH > 2. Near pH 2, $FeH_2AsO_4^{+2}$ is predicted to represent ~ 45 % of total arsenic in solution. This species decreases rapidly in importance as $H_2AsO_4^-$ dominates from 20 % at pH 2 to ~ 90 % at pH 5 (Fig. 34 and 35).

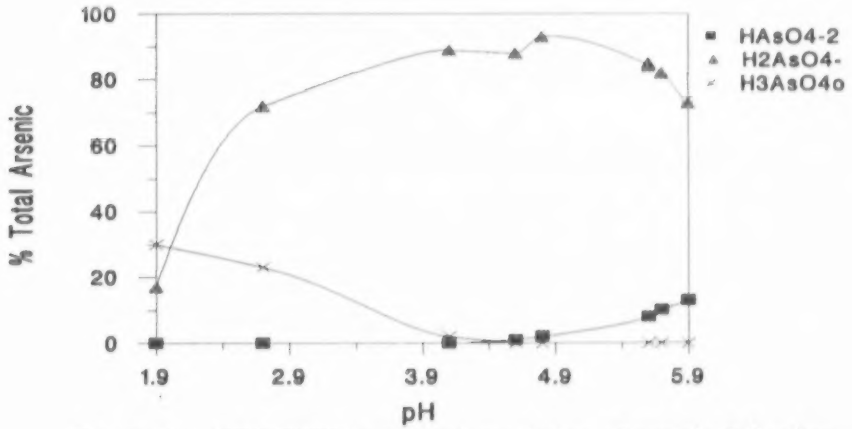


Figure 34. GEOCHEM predicted speciation of arsenic following adsorption.

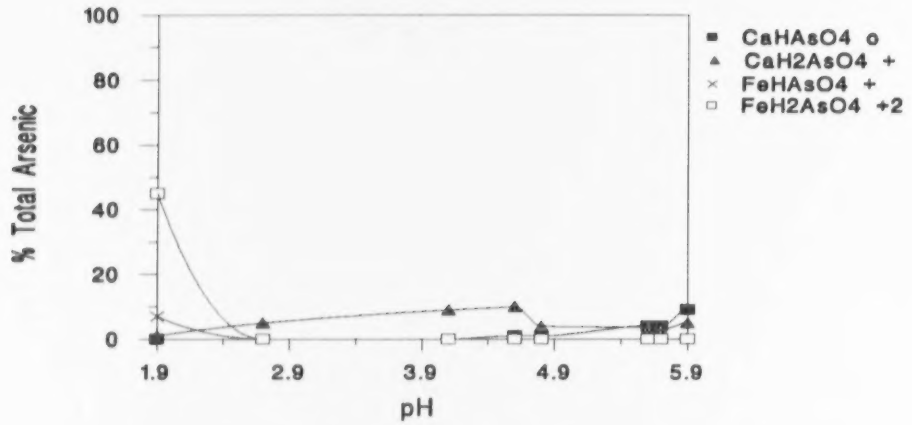


Figure 35. GEOCHEM predicted speciation of arsenic following adsorption.

O'Neill (1990) showed in his work that the adsorption envelope for As occurs at about pH 4 as $H_2AsO_4^-$ species which agrees with this study (Fig. 35). Elkhatib, et.al. (1984) also studied arsenic adsorption and showed that sorption by clay minerals increased with increased pH to a maximum at pH 7. They also identified increases in sorption with increases in Fe_2O_3 (s) content. All studies show rapid, high energy adsorption with little if any desorption. Frost and Griffen (1976) showed maximum As sorption at pH 5 for both kaolinite and montmorillonite and showed that adsorption follows the speciation curve for $H_2AsO_4^-$ ion indicating that this is the principle adsorbed ion. Speciation also showed that some $FeH_2AsO_4^{+2}$ was present under acid conditions and may be mobile.

Results indicate that arsenic should not pose a threat to the environment under phosphogypsum waste repositories. The element is significantly attenuated and would not adversely affect groundwater quality.

iii. Cadmium Precipitation

Cadmium is an element of particular concern in assessing possible environmental contamination by leaching process water at phosphogypsum waste

repositories. Phosphogypsum, as well as the sluice water, have been found to contain elevated levels of Cd over background. Results show that initial Cd concentration in solution was 2.1 mg L^{-1}. Soluble cadmium levels appear to be very pH dependent. Soluble levels vary from 1.6 to 2.1 mg L^{-1} at pH < 3.5 (Fig. 36). At pH > 3.5 solution Cd drops to 0.05 mg L^{-1} at pH 5.5. At pH > 5.5 there is virtually no Cd present in solution.

As the results show Cd distribution between solid and solution phase is pH dependent which concurs with work of Christensen (1989). For strongly acidic pH values, Cd remains relatively soluble (Fig. 36). For these acidic conditions, Cd is found mainly as Cd^{+2} and to a lesser extent as $CdSO_4^o$ species (Fig. 38). This agrees with McBride (1980) who found soluble Cd mainly as bioavailable Cd^{+2}. Speciation is important in determining bioavailability. Plant uptake from soil and groundwater is much lower in alkaline than acid environments and Cd^{+2} is found to be the most available and mobile species (Hirsh and Banin, 1990).

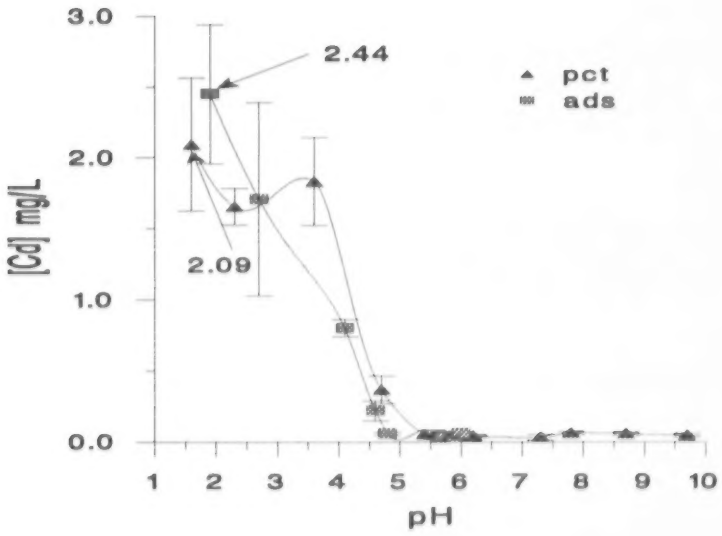
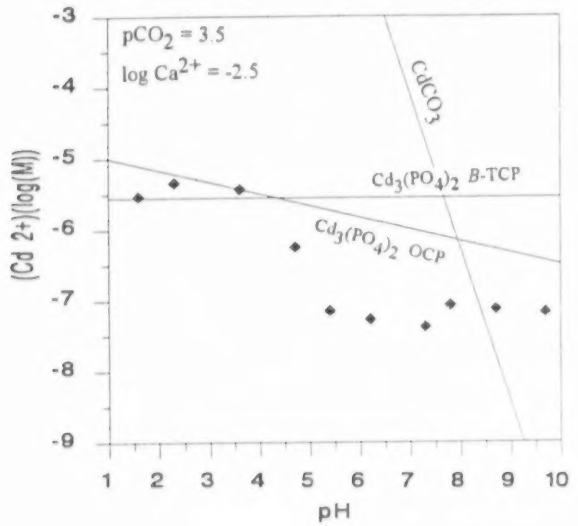


Figure 36. Soluble cadmium concentration (mg L^{-1}) versus change in pH.

Solubility controlling solids may exist for Cd, but the data do not match predicted concentrations based on known solubility controlling solids (Fig. 37). Cadmium ion activities at pH < 3.5 are near -5.5 log Molar. $Cd_3(PO_4)_2$ (s) could be the solubility control for these strongly acidic conditions. Between pH 4 and 8.5 Cd ion activities are below the $Cd_3(PO_4)_2$ OCP and $CdCO_3$ (s) mineral solubility lines. The solution is undersaturated with respect to these minerals. At pH 8.5 the solution appears to be oversaturated with respect to $CdCO_3$ (s).



Thermodynamic data from Lindsay (1979).

Figure 37. Solubility equilibria of some cadmium minerals with neutralization data.

If solubility controlling solids exist, it is possible to predict maximum soluble equilibrium metal concentrations. The results indicate that in the acidic samples $Cd_3(PO_4)_2$ (s) could be the solubility control (Fig. 37). For pH values > 3.5, no known solubility controlling solids match the data. Work done by Street, et.al. (1977 and 1978) found that octavite ($CdCO_3$ (s)) limited soluble Cd in soils at pH > 7.5 and that chemisorption of $CaCdCO_3$ (s) and $CdCO_3$ (s) are important attenuation controls. The similar ionic radii of Ca^{+2} and Cd^{+2} at 0.100 nm and 0.095 nm accounts for Cd^{+2} replacement of Ca^{+2} on calcite surfaces. Chemisorption of Cd^{+2} appears to be an important mechanism in attenuating

soluble Cd (M^{c}Bride, 1980). Calcareous soils are therefore successful in reducing Cd levels in solution and contribute to attenuation of Cd.

Permitted application rates of Cd containing wastes are twice as high on calcareous soils as on non-calcareous soils due to carbonate minerals having direct and indirect effects on heavy metal mobility (Papadopoules and Rowell, 1988). Papadopoules and Rowell (1988) determined that precipitation / dissolution is more important in controlling Cd levels at high Cd concentrations and that at low Cd concentrations adsorption / desorption may be more important.

Cadmium speciation identifies both Cd^{+2} and $CdSO_4^{o}$ as important ion pairs. These two species are distributed as follows: 50-70% Cd^{+2}, 30-50% $CdSO_4^{o}$ at pH < 4.5 and 65% $CdSO_4^{o}$, 5% Cd^{+2} at pH > 4.5 (Fig. 38). At pH > 9, $CdOH^{+}$ is present as approximately 10% of the total Cd.

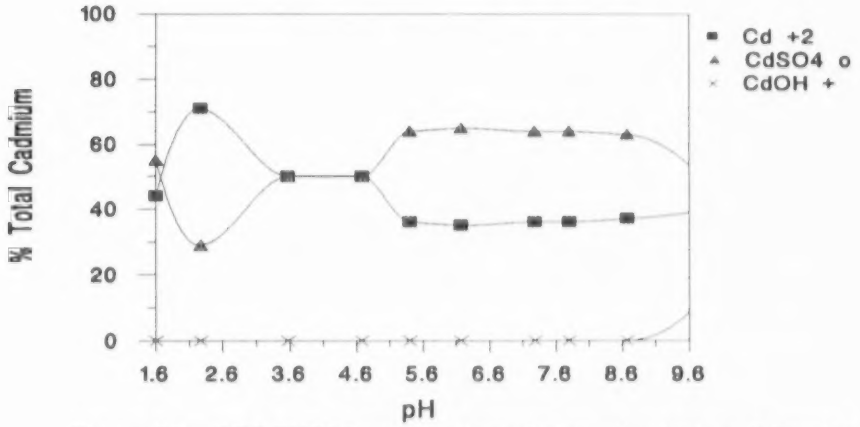


Figure 38. GEOCHEM predicted speciation of cadmium following neutralization.

iv. Cadmium Adsorption

Attenuation of Cd by adsorption occurred through the pH interval of 2.5 to 5 (Fig. 39). Maximum adsorption occurred at pH 3.5. At pH > 5.5, all detectable Cd had chemically precipitated and sorption is not relevant. For pH values < 2.5, final Cd concentrations exceeded levels in solution at the on set of the adsorption experiment, possibly due to dissolution and release of Cd from the soil.

The adsorption experiment again outlines the importance of pH on Cd attenuation. Most work done on Cd has illustrated the sensitivity of pH on sorption. In polluted soils adsorption processes rather than precipitation appears to control the distribution of Cd between solute and soil (Alloway, 1990). Results of this study show the greatest adsorption to be around pH 3.5 (Fig. 40). This pH value is lower than some other studies which show maximum sorption around pH 4 - 7 (Christensen, 1984; and Alloway, 1990). One study by Garcia-Miragaya and Page (1978) found an increase in adsorption on montmorillonite at pH 3.7. They concluded this was due to an increase in fresh, amorphous, highly reactive materials such as silicic acid and Al-silicic acid mixes which resulted from montmorillonite decomposition at this pH. This may be occurring in this study resulting in the adsorption maximum at pH 3.5. Cadmium is found as cationic Cd^{+2} and $CdSO_4^o$ species (Fig. 40) and hence adsorption may be facilitated by speciation effects with the free ion (Cd^{+2}) accounting for the sorption reaction.

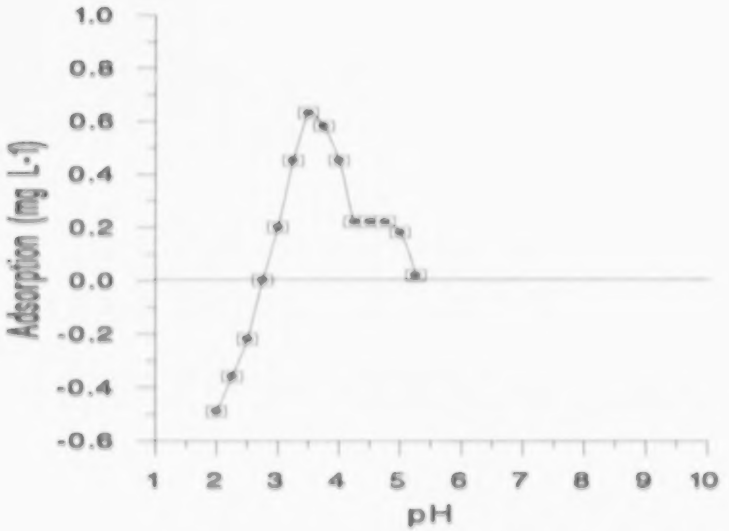


Figure 39. Adsorption curve for cadmium in relation to solution pH.

Cadmium speciation of the aqueous phase of the sorption experiments is very similar to that after precipitation. Figure 40 shows that both Cd^{+2} and $CdSO_4^o$ species are important. At pH < 3.5 and > 4.7 $CdSO_4^o$ represents a predicted 50-60% of total Cd while Cd^{+2} represents 40-50%. Between pH 3.5 and 4.7 Cd^{+2} is increased to 50-60% while $CdSO_4^o$ is 40-50% of total Cd.

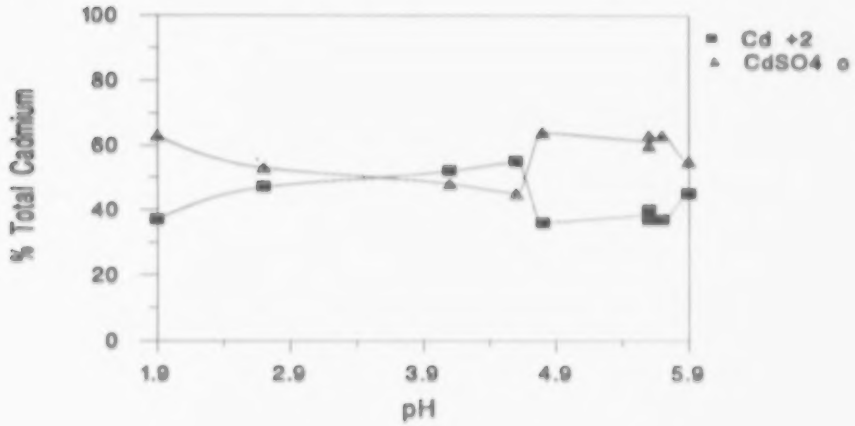


Figure 40. GEOCHEM predicted speciation of cadmium following adsorption.

These results indicate Cd is effectively attenuated by precipitation and adsorption. This finding is consistent with the conclusions of Luther (1991) who studied trace element attenuation for phosphogypsum leachates. Results of this study suggest subsurface migration of Cd below waste repositories should not pose a major environmental problem.

v. Chromium Precipitation

Figure 41 illustrates chromium solution concentration versus pH for both precipitation and adsorption experiments. At an initial pH of 1.6, concentration of Cr is 1.8 mg L^{-1}. This concentration drops abruptly with an increase in pH to pH 4. At pH > 4 the concentration of Cr is < 0.1 mg L^{-1} for the precipitation experiment.

Studies done on fly ash by Rai and Szelmeczka (1990) found Cr (III) instead of Cr (VI) to dominate in both aqueous and solid form. In the trivalent form, Cr can be expected as Cr^{+3} or CrO^{-2}. Under highly oxidized conditions hexavalent Cr can be found as $Cr_2O_7^{-2}$ or CrO_4^{-2}. Studies have also shown Cr (III) complexes to be dominant in natural waters (Rai, et. al., 1987). Chromium (III) is less toxic and less mobile than its hexavalent form. There have been reports of groundwater contamination by Cr (VI) (Bartlett and Kimble, 1976b) and an amount in excess of 1.7 mg L^{-1} in effluent water exceeds certain regulatory limits. There is concern over oxidation of Cr (III) to Cr (VI) which could result in increased toxicity and mobility of chromium.

Results of this study have shown that Cr would not be readily transported in natural environments which have pH in the range of 5 to 10. Our study shows that concentrations of soluble Cr decreases substantially at pH > 2.5 (Fig. 41). Chromium shows the greatest solubility at pH 2 and greatest insolubility and complete attenuation at pH > 4.5. Solubility diagrams illustrate that precipitation of (Cr, Fe)$(OH)_3$ solid solution compounds may be the control in precipitation reactions (Fig. 42). Studies by Sass and Rai (1987) and Rai and Szelmeczka (1990) showed results whereby neutralization of acidic solutions containing both Cr (III) and Fe (III) resulted in co-precipitation of $(Cr_xFe_{1-x})(OH)_3$ (s) between pH 2 - 6. Co-precipitation of Cr and Fe are due to similar ionic radii of 0.063 nm and 0.064 nm, respectively. Chemical precipitation appears to be effective in reducing soluble Cr levels.

For the purpose of this study it is assumed that all chromium was present in the trivalent state. This assumption is supported by the work of Rai et.al. (1987). Solubility controlling solids may play an important role in Cr solubility under all conditions. At acidic and neutral pH's $(Cr_xFe_{1-x})(OH)_3$ (s) may be the controlling solid (Fig. 42). While the data points do not match one of the solubility isolines, the trend in the data are consistent with a high Cr mole fraction solid solution of (Cr,Fe)$(OH)_3$ (s).

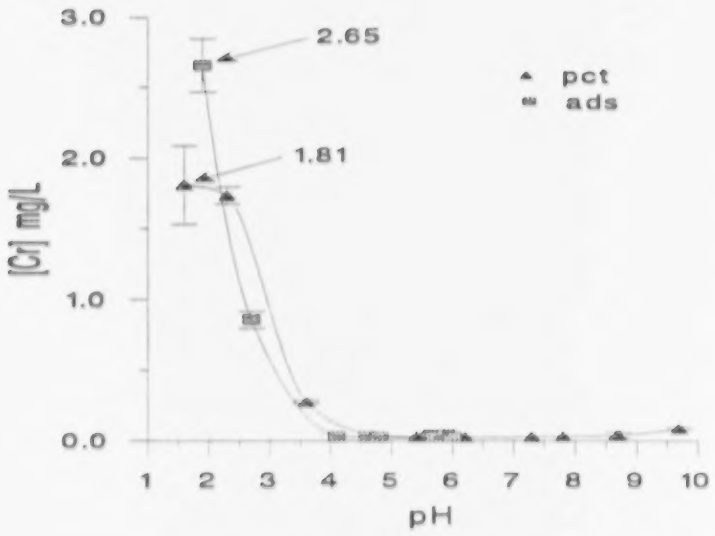
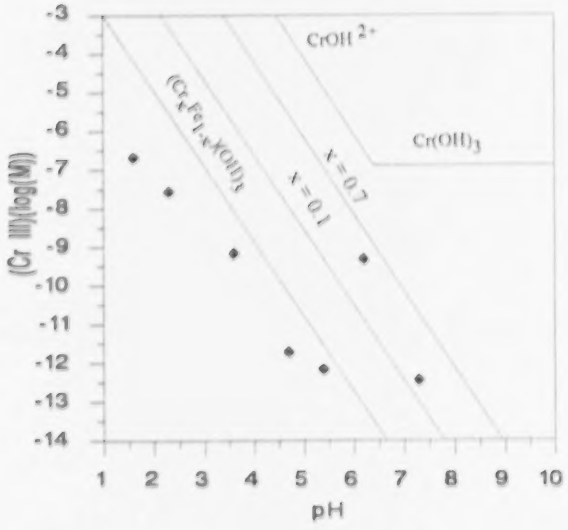


Figure 41. Soluble chromium concentration (mg L^{-1}) versus change in pH.



Thermodynamic data from Rai, et.al. (1984), and Rai, et.al. (1987).

Figure 42. Solubility equilibria of some chromium minerals with neutralization data.

In the pH range of maximum Cr solubility, CrF_2^+ is the dominant form of chromium. This ion pair dominates at 100% of the total Cr at pH < 2.6 (Fig. 43). As pH increases $CrH_2(PO_4)_2^-$ becomes the dominant species and is expected to be the prevalent species under normal soil solution conditions at pH 2 - 6 (Rai, et. al., 1987; Sass and Rai, 1987; and Rai and Szelmeczka, 1990). Phosphogypsum sluice water contains significant amounts of residual phosphoric acid and this PO_4^{-3} plays an important role in speciation.

Speciation of chromium as predicted by GEOCHEM (Figs. 43-45) illustrates that in the pH range of elevated Cr concentrations CrF_2^+ is the dominant ion pair. CrF_2^+ remains dominant up to pH 3. Chromium phosphate as $CrH_2(PO_4)_2^-$ is prevalent from pH 3 to 6. At pH > 6 $CrCO_3$ species, especially $Cr(CO_3)_2^-$ and $Cr(CO_3)_3^{-3}$ become dominant species.

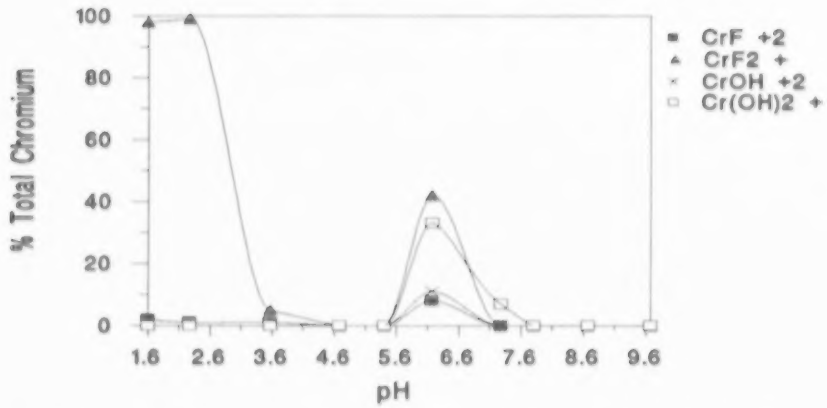


Figure 43. GEOCHEM predicted speciation of chromium following neutralization.

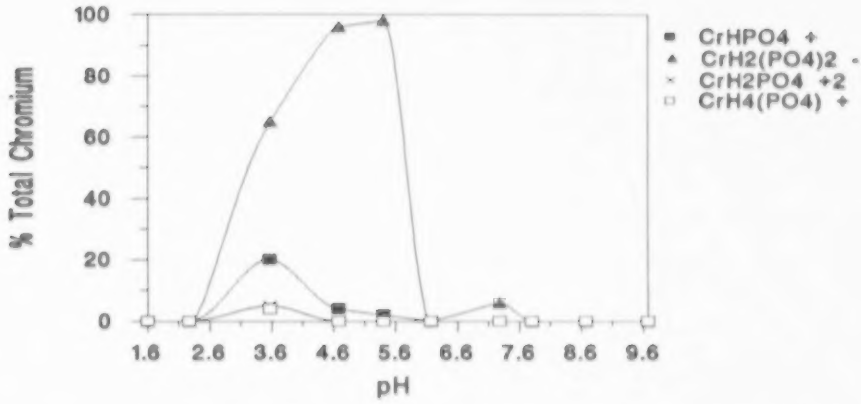


Figure 44. GEOCHEM predicted speciation of chromium following neutralization.

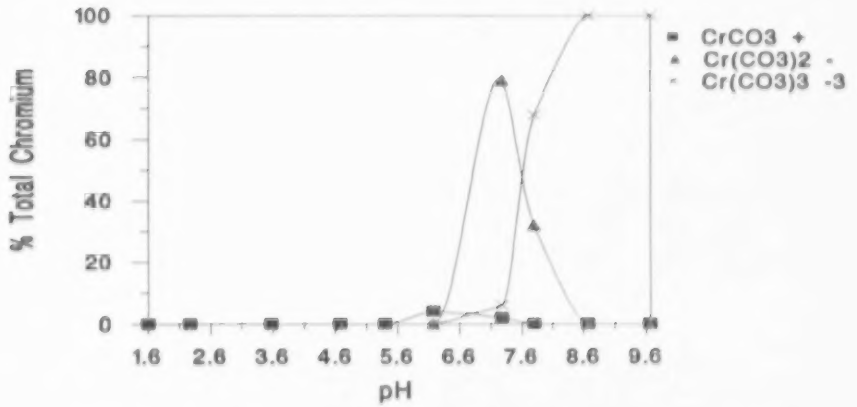


Figure 45. GEOCHEM predicted speciation of chromium following neutralization.

vi. Chromium Adsorption

Figure 41 shows adsorption is also pH-dependent. There is a sharp decrease in solution concentration from 2.65 mg L^{-1} to 0.05 mg L^{-1} from pH 2.65 to 4. Figure 46 shows adsorption is most prominent between pH 2.5 and 3. At this pH range approximately 0.4 to 0.5 mg L^{-1} Cr is adsorbed. Some negative

adsorption or dissolution of native Cr in soil occurs at pH 2. At pH > 3 adsorption drops off and at pH 4.75 there is no Cr in solution (Fig. 41).

The results show adsorption also plays a role in attenuation of Cr although it does not appear to be as important as precipitation. Figure 46 shows that adsorption further decreases soluble Cr concentration above pH 2. The clay fraction of the soil used in the experiment consists of phyllosilicates and iron oxides; both groups of minerals are known to adsorb chromium. Adsorption on oxides is greater than sorption on montmorillonite at all pH's (Zachara, et.al., 1989). Studies have also shown there to be competition between negatively charged chromium species and SO_4^{-2}, HCO_3^-, $H_2PO_4^-$, and HPO_4^{-2} (Stollenwerk and Grove, 1985). In this experiment, at the lowest pH values, positively charged chromium species would compete with H^+ for adsorption sites. As pH decreases, sorption of positively charged chromium species should increase as is the case (Fig. 46).

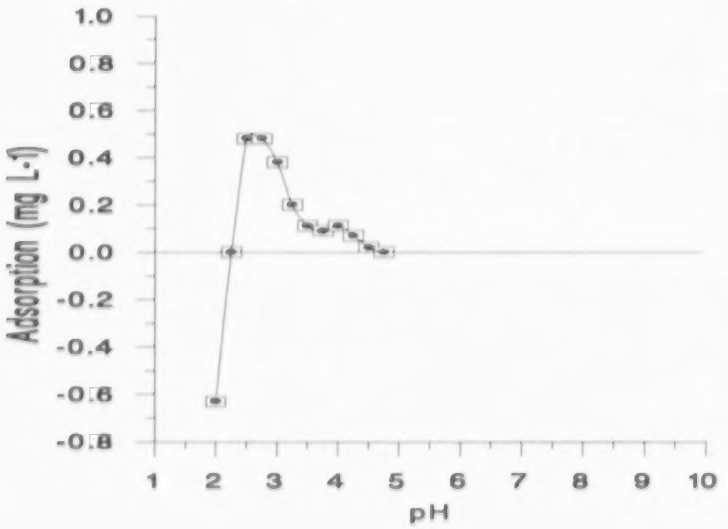


Figure 46. Adsorption curve for chromium in relation to solution pH.

Results of speciation following adsorption is illustrated in figures 47 - 49. The important pH range in which to consider speciation is at pH 1.9 - 4. Beyond pH 4 the solution concentration of Cr is minimal. Up to pH 3 the dominant

species is CrF_2^+ at 80%. At pH >3, CrF_2^+ decreases and loses dominance to $CrH_2(PO_4)_2^-$ which dominates from pH 3.5 to 5.5. At pH > 5.5 $Cr(CO_3)_2^-$ is the important species but total soluble concentration of Cr is nearly inconsequential.

Speciation following adsorption again shows an abundance of chromium fluorides, mainly CrF_2^+ (Fig. 47). This species and $CrH_2(PO_4)_2^-$ may only pose a problem in the acidic range due to almost complete precipitation of chromium at pH 4.75 and beyond.

Results of the precipitation and adsorption experiments indicate that Cr would be nearly completely attenuated as sluice water reacts with calcareous subsoils. Chemical precipitation, probably as an Cr-Fe hydroxide, largely controls solution concentrations. Impact on the environment should be minimal in terms of chromium loading.

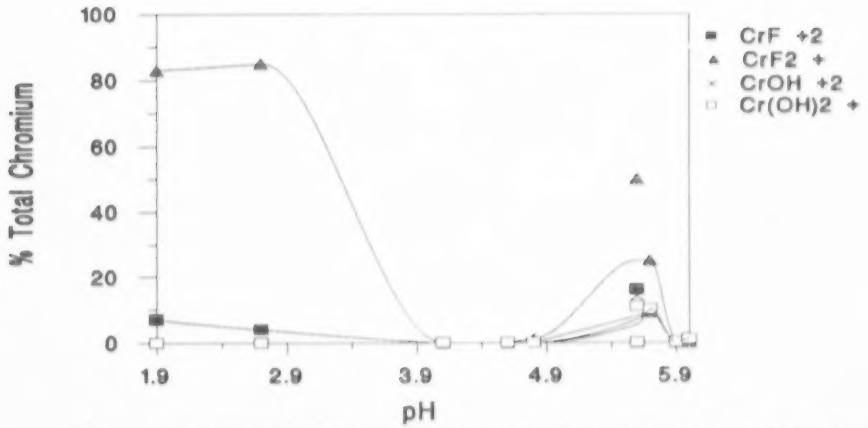


Figure 47. GEOCHEM predicted speciation of chromium following adsorption.

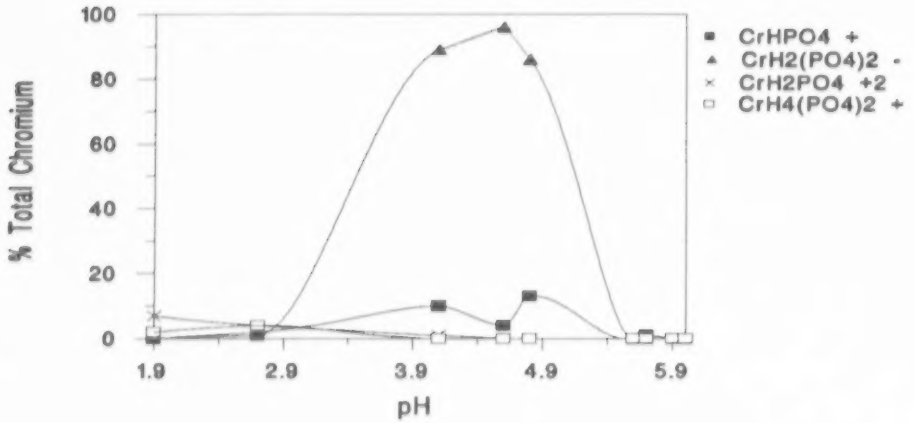


Figure 48. GEOCHEM predicted speciation of chromium following adsorption.

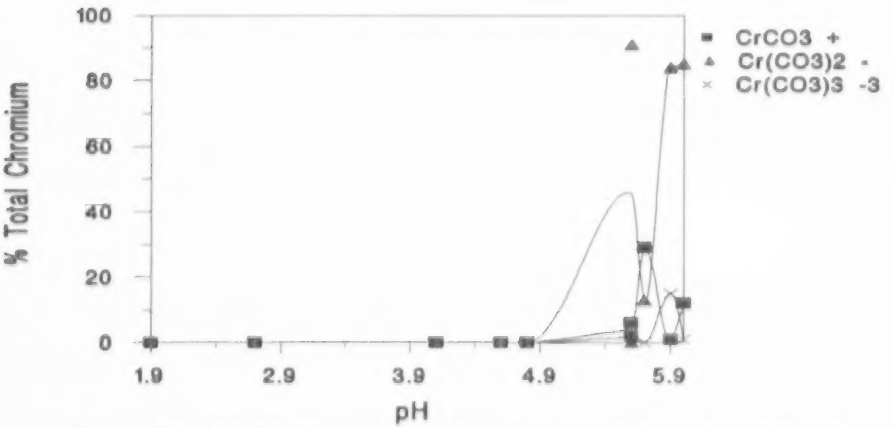


Figure 49. GEOCHEM predicted speciation of chromium following adsorption.

vii. Selenium Precipitation

Chemical neutralization of sluice water results first in a drop in selenium concentration from 0.70 to detection limits. The drop in concentration is nearly linear with pH to pH 5 (Fig. 50). As the pH of the neutralized sluice water

increased above pH 5, an increase in Se solubility is seen and at pH > 6 selenium concentrations in solution are approximately 0.25 mgL^{-1}.

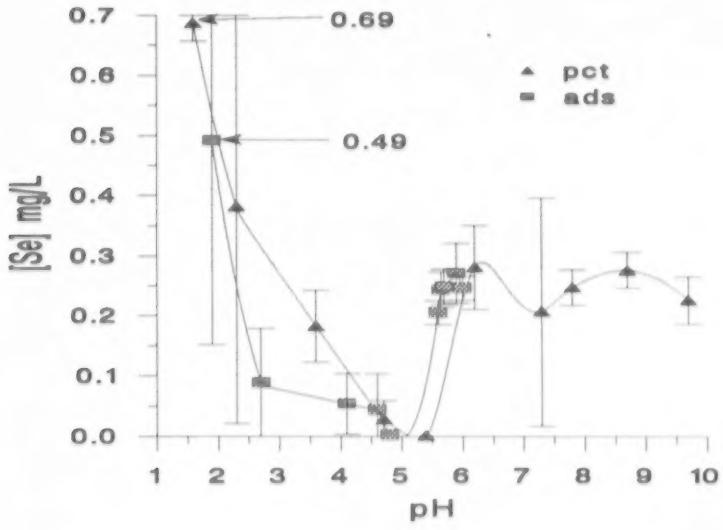


Figure 50. Soluble selenium concentration (mg L^{-1}) versus change in pH.

Selenium, as with arsenic and chromium, is highly dependent on redox status. As previously discussed, oxidizing conditions are expected under a waste leaching environment. Previous work done on phosphogypsum (Luther, 1991), fly ash (Elrashidi, et. al., 1987), and soils (Alrichs and Hossner, 1987) have indicated that both selenate (Se VI) and selenite (Se IV) occur. Eh-pH diagrams (Elrashidi, et. al., 1987) illustrate that selenite is the most common species of selenium in moderately oxidized conditions (pe+pH 7.5 - 15). Studies have also shown under these conditions the primary species of Se IV are $HSeO_3^-$ and SeO_3^{-2}. These species are expected to be the dominant selenium species found in the phosphogypsum sluice water. The conditions in seep water and cooling reservoirs as well as in the solid waste are expected to be similar (Elrashidi, et. al., 1987).

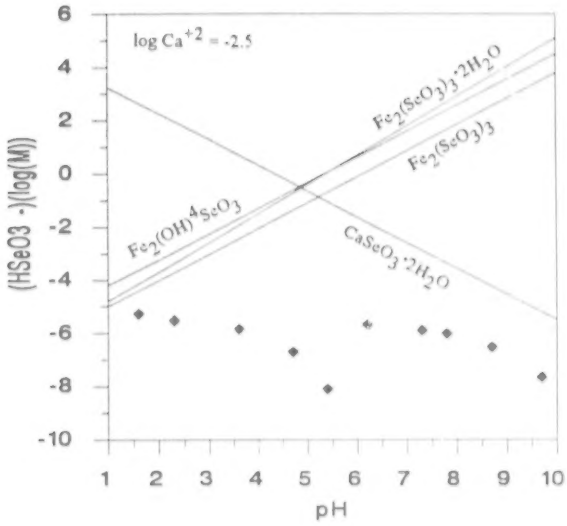
The behavior of soluble Se is again influenced by solution pH values. Alrichs and Hossner (1987) found selenium to be mobile at most pH's with the most rapid movement and leaching occurring at pH 7 - 9. There was also

abundant movement of Se at pH 2 and the least was evident at pH 3 which agrees with results shown in this study. Selenium attenuation reaches a maximum at pH 5 (Fig. 50). This study shows that under both acidic and near neutral to alkaline pH's, Se does display aqueous solubility. In these pH ranges Se is found at concentrations of 1 to 1.5 orders of magnitude greater than allowed in drinking water.

A selenium solubility controlling solid diagram using hydrogen selenite ($HSeO_3^-$) which is the dominant ion in medium oxidized systems under both acid and neutral pH conditions (Eary, et. al., 1990) is constructed (Fig.51). Figure 51 identifies iron selenite compounds and a calcium selenite compound as possible solubility controls. Results illustrate that selenium is undersaturated relative to these potential controlling solids. Thus, there is insufficient selenium in solution to invoke a solubility controlling solid.

Most selenate and selenite solids are too soluble to act as solubility controlling solids for selenium under oxidizing conditions expected for certain waste leaching environments (Rai, et. al., 1987). There is limited information on selenium solubility in soil environments for varying redox conditions. This study further exemplifies the importance of pH on solubility. The results illustrate that Se solution concentration are undersaturated with respect to any predicted solubility controls. Possible selenite minerals which could act as solubility controls are $MnSeO_3$ (s) which has been found to be the most stable selenite in near neutral to acid soils while in alkaline soils $PbSeO_3$ (s) is the most stable mineral (Elrashidi, et. al., 1987). In this study the concentrations of important ions involved in the formation of these minerals, Mn^{+2}, Pb^{+2}, SeO_3^{-2}, are too low for the minerals to form (Fig. 51). Other selenite minerals are too soluble to form in soil and waste repository environments. Under highly acidic conditions $Fe_2(OH)_4Se)_3$ (s) has also been predicted as a solubility control (Bar -Yosef and Meek, 1987) but again this is not evident in this study which agrees with work done by Elrashidi, et. al. (1987) in that iron selenite compounds are not expected to be controls. In the absence of solubility controlling solids, adsorption may be the mechanism of concentration control. However, the fact that Se concentrations decrease in the precipitation experiment indicates that some unknown solubility controlling solid is involved at least for pH values 2 to 5. Both adsorption and

precipitation are dependent on the nature of the aqueous species of the element selenium.



Thermodynamic data from Elrashidi, et.al. (1987), Rai, et.al. (1984), and Lindsay (1979).

Figure 51. Solubility equilibria of some biselenite minerals with neutralization data.

As indicated, for the conditions of the sluice water, i.e. oxidized and acidic, selenium speciates as selenite. Selenite (SeO_3^{-2}) is largely combined with H+ with the relative proportions decreasing with increasing pH. The degree of complexing can be seen in Figure 52. Under highly acid conditions (pH 1.6 - 4.0) $H_2SeO_3^o$ is dominant. At pH > 4, $HSeO_3^-$ dominates and remains at 100% of Se up to pH 6. As the pH increases further the proportion of $HSeO_3^-$ decreases and other species ($CaSeO_3^o$ and SeO_3^{-2}) predominate. The behavior of environmentally sensitive trace elements is considerably influenced by speciation. Using GEOCHEM, selenium is predicted to form ion pairs that are either neutral or anionic in charge. Figure 52 illustrates the range that these species dominate. Results here compare to other work done on fly ash and soils in that selenite is

readily complexed with H^+. It is expected that below the pK1 of $HSeO_3^-$ at 2.75, $H_2SeO_3^o$ will dominate, and above the pK2 of 8.5, SeO_3^{-2} will dominate (Ahlrichs and Hossner, 1987). Our results show $H_2SeO_3^o$ dominates up to pH 4. Free ion selenite SeO_3^{-2} dominates at pH > 8.2. In general, $HSeO_3^-$ is the major species under acidic and neutral pH ranges expected for most soil environments. Results of this study suggest $HSeO_3^-$ to be the species of selenium available for plant uptake or possible migration. Some speciation involving ion pairing with calcium occurs due to the large amount of calcium present in neutralized sluice water. Appreciable amounts of selenium are evident at both acidic (pH<3) and near neutral to alkaline (pH>5.5) pH's with the species present being $H_2SeO_3^o$ and $HSeO_3^-$, and SeO_3^{-2} and $CaSeO_3^o$, respectively (Fig. 52). Under the lowest selenium solution concentrations between pH 3 - 5.5, $HSeO_3^-$ is the dominant species.

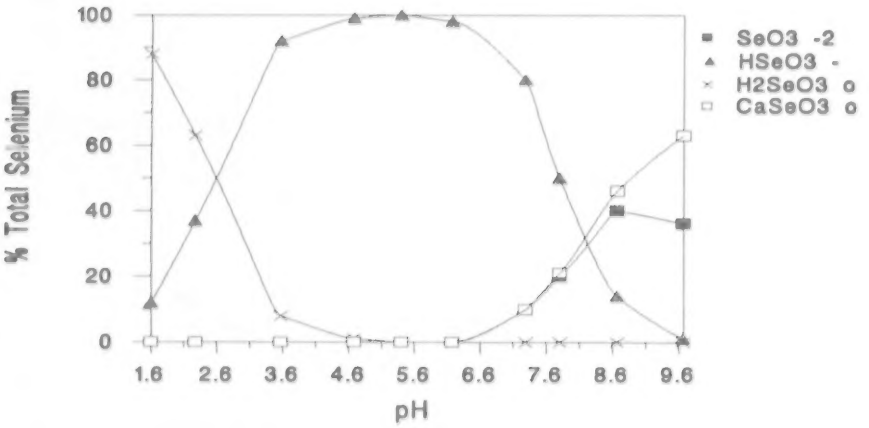


Figure 52. GEOCHEM predicted speciation of selenium following neutralization.

viii. Selenium adsorption

Selenium adsorption onto soils plays a significant role in attenuation. Figure 50 illustrates a more pronounced decrease in Se solution concentration

under acidic conditions than found with chemical neutralization alone. Solution concentration drops from 0.50 mg L^{-1} at pH 2.2 to < 0.1 mg L^{-1} at pH 2.7. With further pH increase to pH 5, attenuation by adsorption becomes less effective. Detection limits are reached around pH 5.0. At pH > 5, an increase in Se solution concentration occurs up to 0.25 mg L^{-1}. The Se concentration appears to level off at 0.25 mg L^{-1} at pH >6. Figure 53 illustrates selenium adsorption. Approximately 0.225 mg L^{-1} Se is adsorbed at pH 2.75. Above and below pH 2.75 Se sorption drops. The least adsorption occurs at pH > 4.5. The figure also illustrates some negative adsorption at pH between 5 and 6 by up to 0.125 mg L-1.

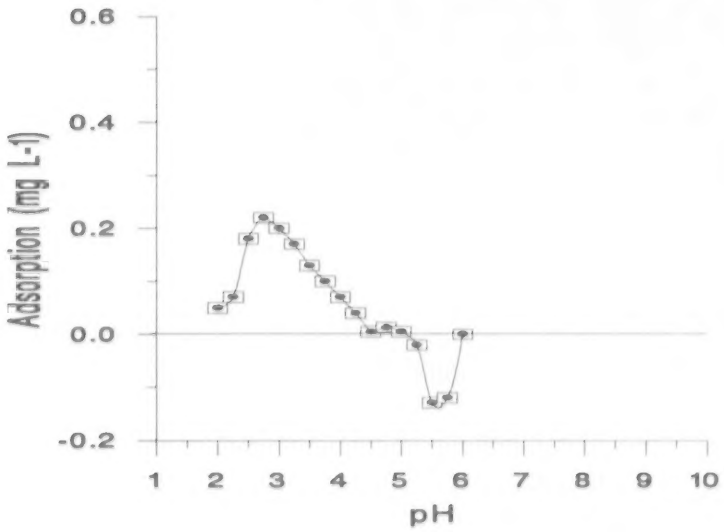


Figure 53. Adsorption curve for selenium in relation to solution pH.

Results of the adsorption experiment agrees with Frost and Griffen (1976) who found that Se (IV) displays an adsorption maximum at pH 2 - 3 then decreases as pH increases. The adsorption of anions such as selenite is greatest under acidic conditions due to positive charge increase on oxyhydroxides below their ZPC (Sposito, 1989). Ahlrichs and Hossner (1987) also describe increased sorption of selenite by ferric hydroxides under acidic conditions. Under acidic conditions, selenite adsorbs by surface ligand exchange similar to phosphate

sorption (Rajan and Watkinson, 1975). Some competition for sorption sites would occur between SeO_3^{-2}, $HSeO_3^-$, PO_4^{-3}, and SO_4^{-2}. Neal, et. al. (1987) found very little competition between SeO_3^{-2}, Cl^-, and SO_4^{-2} but did find PO_4^{-3} competing over the entire pH range. Phosphogypsum sluice water contains significant amounts of both sulfate and phosphates so competing ion affects may also contribute to Se sorption. We still however see adsorption effects.

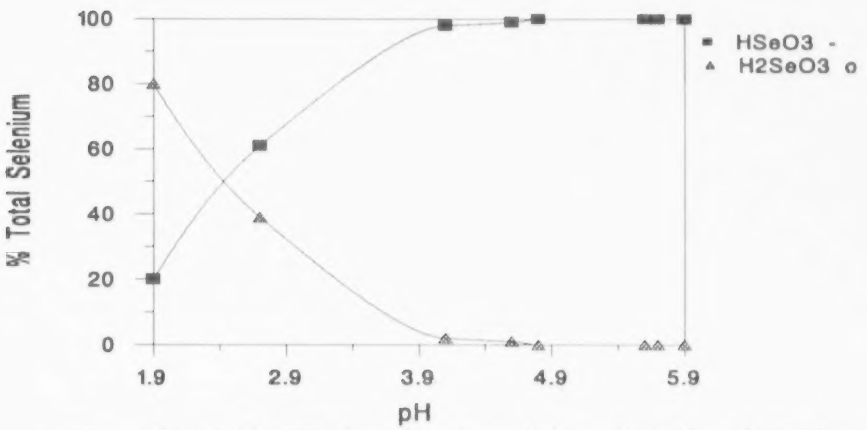


Figure 54. GEOCHEM predicted speciation of selenium following adsorption.

Speciation as predicted by GEOCHEM following the adsorption experiment is similar to chemical neutralization results (Fig. 54). The speciation diagram is restricted to the pH range found in the adsorption experiment (2 - 6) and in this range SeO_3^{-2} is complexed with only hydrogen as either $HSeO_3^-$ or $H_2SeO_3^o$. Neutral H_2SeO_3 dominates for pH $<$ 2.5 while $HSeO_3^-$ replaces $H_2SeO_3^o$ at pH $>$ 2.5 and at pH $>$ 4 makes up 100% of total selenium in solution.

Biselenite $HSeO_3^-$ is the dominant species throughout the pH range and thus the dominant adsorbed species as well. $HSeO_3^-$ is thought to exchange with OH^- at sorption sites. Also under highly acidic conditions neutral H_2SeO_3 is present.

The results for attenuation of selenium is of particular relevance in terms of environmental issues. Results (Fig. 50) show that selenium levels in the initial sluice are 0.70 mgL^{-1} whereas the Canadian and U.S. drinking water standards (DWS) are 0.01 mgL^{-1} and the USEPA maximum effluent contamination concentration is set at 1.0 mgL^{-1}. Selenium originating from sluice water may intrude groundwater below waste repositories. Concentration may exceed water quality guidelines.

CHAPTER V

SUMMARY AND CONCLUSIONS

The objectives of this study were to characterize the leaching properties of phosphogypsum sluice water from the phosphoric acid plant in central Alberta. The information obtained is applicable to all related production processes and waste streams. The study is specific in that it characterizes wastes produced from Togo phosphate rock. Each rock source has its own properties and level of contaminants which contribute to the contaminant levels found in the product acid and waste materials. However the behavior of elements in the sluice water, such as the trace elements of this study, is not dependent on the source of the phosphate ore.

Past studies have focused on the solid phosphogypsum. These studies provide information on characteristics of the more benign solid waste. Contaminant content in the phosphogypsum are usually less than in the sluice water. Additionally, a significant portion of the contaminant contained in phosphogypsum originates in the sluice water contained in the pore space of phosphogypsum. As a consequence, if there was to be leaching off site, the major contaminant load would be found in the sluice water itself. This is the waste material which is likely to cause the most significant negative environmental impact. Very few studies have been done on this sluice water and thus this study represents original research.

This study identified sulfate, fluoride, radionuclide U-238, and the trace elements arsenic, cadmium, chromium, and selenium as the elements of concern. Sluice water acidity is another detrimental characteristic. The concentrations of the elements of concern in sluice water are 8600 mg L^{-1} for sulfate, 4700 mg L^{-1} for fluoride, and 2.5 mg L^{-1} or 36 BqL^{-1} for U-238. The trace element concentrations are: arsenic 1.3 mg L^{-1}, cadmium 2 mg L^{-1}, chromium 1.8 mg L^{-1}, and selenium 0.7 mg L^{-1}. All these contaminant levels are elevated over both Canadian and U.S. drinking water and maximum contaminant levels by 1 to 3 orders of magnitude.

This study was directed at examining attenuation of the elements of concern. The major mechanisms of precipitation/dissolution and adsorption / desorption were assessed in the evaluation of chemical attenuation.

The major conclusions and concerns that can be drawn from this research are:

1) The acidity of the sluice water is a definite concern. At pH 1.6 the sluice water is far below regulatory limits of pH 6.5-8.5. This low pH carries with it high levels of soluble salts and trace elements. The high acidity may also cause problems with liners underlying waste repositories. Degradation of clay and synthetic liners would increase off site migration of the sluice water into groundwater regimes. This study recognizes the need for neutralization of the sluice water to reduce potential environmental contamination.

2) Sulfate levels found in the sluice water are significantly high and may be mobile under acidic conditions. Chemical neutralization appears to be the major removal mechanism resulting in precipitation of gypsum. Both precipitation and reaction with soil minerals reduce sulfate levels in solution although results of this study show that attenuation may not be sufficient to reduce sulfate levels below regulatory limits.

3) Sluice water before neutralization contains extremely high levels of fluoride (4700 mg L^{-1}). While chemical precipitation reactions, largely as CaF_2 precipitation, decreases soluble F- levels considerably, solution concentrations are likely to remain at about 13 mg L^{-1}. This concentration exceeds certain water quality guidelines. Considering the results of speciation and for the adsorption study, there is potential for some subsurface migration of fluoride. Immediately below waste repositories, soil material is likely to be strongly acidified by reaction of infiltrating sluice water. Soil mineral stability is likely to be affected in the zone of infiltration of sluice water warranting concern.

4) Uranium present in the sluice water will only be of concern if the solution is maintained in an acidic state. Under acidic conditions both negatively charged and neutral uranium fluoride complexes may be problematic.

5) Attenuation of trace elements arsenic, cadmium, and chromium effectively reduce soluble levels below regulatory limits set by both Canadian and

United States regulatory agencies. Both arsenic and cadmium should pose no threat to the environment at pH > 5. At this pH chemical precipitation of As with Fe and Al minerals, and precipitation of Cd-Ca minerals is suspected. Chromium is almost completely attenuated at pH > 4.5 due to precipitation reactions most likely as Cr-Fe compounds.

6) Selenium is one element which may require further attention. Initial concentrations of 0.7 mgL^{-1} are 70x higher than regulatory limits. Between pH 3.5 and 6 we see high attenuation of the element while outside this pH range Se could be an environmental problem. Under Alberta soil conditions where calcareous subsoils will likely increase pH of infiltrating sluice water to pH 7-8.5 there may be some leaching of selenium at levels around 0.25 mg L^{-1}.

7) The information attained from this study can be used on a generic foundation. The sluice water at all phosphate producing plants throughout the world are similar in characteristics and would thus have the same inherent problems. Information is compiled on laboratory study of both chemical neutralization and reaction with soil minerals and depending on the environmental conditions within the vicinity of the waste repositories possible final sluice water elemental concentrations can be predicted. The conclusions in this study will work well for Alberta subsurface conditions with an abundance of calcareous minerals but for other environments, such as phosphate plants in Florida, with different soil conditions, conclusions will vary as to the leachability of the sluice water major and trace elements and radionuclides.

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